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REPORT No. ER-5159

THE REDUCTION OF CARBON DIOXIDE USING A FLUIDIZED CATALYST BED

UNCLASSIFIED

FINAL REPORT

Office of Naval Research
Contract No. Nonr 3431(00)(FBM)

DECEMBER 15, 1962

TAPCO
A DIVISION OF
Thompson Ramo Wooldridge Inc.
CLEVELAND, OHIO

ABSTRACT

Carbon dioxide is reduced by hydrogen to carbon and water, using a fluidized catalyst bed. This system, applied to submarine atmosphere control, will make it possible to avoid the venting of hydrogen and carbon dioxide overboard, a practice that could have serious consequences from the standpoint of detection and future deep diving submarine systems design. In addition, the fluidized bed concept has shown considerable success from the viewpoint of continuous carbon removal from the system.

Tests were made on a one man capacity system in which the reaction gases were continually recycled at approximately atmospheric pressure. Water was removed by condensation and fresh feed (2 moles of hydrogen per mole of carbon dioxide) was added as required. Under normal operating conditions the ratio of recycle rate to reaction rate is about 7.7. Carbonyl iron powder was found to be an excellent catalyst for this reaction. Reaction rates up to 350 volumes of reaction gas per volume of catalyst per hour were observed at a reactor temperature of 1100°F. At this rate 0.66 cu. ft. of catalyst would be required to reduce the carbon dioxide produced by a 100 man crew.

With carbonyl iron catalyst at 1100°F, the maximum reaction rate was obtained when the recycle gas composition was kept hydrogen rich at about four atoms of hydrogen per atom of oxygen. Removing all of the water from the recycle gas more than doubled the reaction rate under some conditions. Reaction rate is an exponential function of temperature up to about 1050°F beyond which it starts to level off. It shows a maximum at 1200 to 1300°F.

A preliminary design of a 100 man capacity carbon dioxide system has been made. The system is estimated to have a weight of 455 lbs and a volume of 31 cu. ft. The power consumption for operating the equipment is estimated at 2.5 Kw.

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1.0 INTRODUCTION

This is a final report on the work carried out at Thompson Ramo Wooldridge Inc. under Phase 2 of Contract Nonr 3431(00)(FBM). This contract is for research work on an Electrolytic Gas Reactor System for submarines. The overall system is to consist of an electrolytic cell that decomposes water to produce hydrogen and oxygen and a reactor to reduce carbon dioxide with hydrogen. The oxygen will be used for respiration by the submarine crew, who will produce carbon dioxide which will be reacted with the hydrogen to produce carbon and water. Such a system is at least partly closed since oxygen and hydrogen are recycled. Food eaten by the crew introduces carbon and hydrogen into the system. The carbon is recovered and stored as elemental carbon, while the hydrogen is converted into water. Two advantages of such a system are that; (1) it makes it unnecessary to reject hydrogen or carbon dioxide overboard, thus avoiding the detection hazards associated with such practices, and (2) reduces the heavy machinery and engineering problems associated with the discharge of waste products to sea at great operating depths.

Since the electrolysis of water is a well-developed process the work under the current contract is concerned with the reduction of carbon dioxide with hydrogen to produce carbon and water. This work has been divided into two phases. In Phase 1, which was carried out between March and December, 1961, various catalysts were tested in a fixed bed. In phase 2, which is now being completed, the reaction is carried out in a fluidized catalyst bed.

The results of Phase 1 were reported in Reference 1. The results of Phase 2 are summarized herewith.

2.0 SUMMARY

This is a final report on the work carried out at Thompson Ramo Wooldridge Inc. under Phase 2 of Contract No. Nonr 3431(00)(FBM). The object of this work was to develop a process for reducing carbon dioxide with hydrogen to produce carbon and water by means of a fluidized catalyst bed, and to make a preliminary design of a 100 man capacity system using the process.

Consideration has been given to the problems associated with the present practice of venting hydrogen and carbon dioxide overboard. It appears that the engineering problems associated with the practice will increase markedly as the operating depth of submarines increases. An even more serious problem is believed to be the detection hazards incident to introducing foreign gases into the sea water. This looks particularly hazardous in the case of hydrogen. It would appear to be a relatively simple matter to make detection devices that could pick up and follow the trail of a submarine that was venting hydrogen overboard.

The reactor employed in the experimental work carried out under Phase 2 of this contract consists of a three inch stainless steel tube that has a porous steel plate near one end that supports the powdered or granulated catalyst. Reaction gases are passed up through the plate at a rate sufficient to fluidize the catalyst bed.

Several catalysts have been tested in this application and two types have been found to have good activity. These are the carbonyl iron powder catalyst and the G-52 catalyst. The carbonyl iron powder is a finely divided high purity iron that is made by the thermal decomposition of iron pentacarbonyl. The G-52 catalyst consists of nickel supported on a refractory oxide. The carbonyl iron catalyst is preferred because it appears to be more active and because its higher density makes it easier to remove the carbon from the reaction zone, without removing appreciable quantities of catalyst. In order to minimize the tendency of iron powder catalyst to loose fluidization and cake before sufficient carbon is formed to coat the metal surfaces, 1% G-52 catalyst has been added to the carbonyl iron catalyst in all tests made on the latter.

Parametric studies have been made on commercial iron catalyst, carbonyl iron catalyst, and G-52. The effect of temperature on the reaction rate shows the typical exponential shape up to about 1050°F, beyond which it tends to level off. It becomes fairly flat in the neighborhood of 1200 to 1300°F. The leveling off is attributed to less favorable equilibrium conditions at the higher temperatures.

An investigation of the effect of recycle gas composition on the reaction rates with carbonyl iron and G-52 catalysts shows that the reaction rate can be correlated with the ratio of hydrogen atoms to oxygen atoms (H/O) in the reaction gas. With the carbonyl iron catalyst at 1100°F, maximum reaction rate is obtained when the H/O ratio is about 4. With G-52 catalyst the maximum rate is obtained at H/O ratios of 2 and 3 for temperatures of 1000 and 1200°F respectively.

Tests on the effect of recycle rate on reaction rate of carbonyl iron catalyst show a straight line effect in which the reaction rate about doubles on increasing the recycle rate from 5.4 to 9.4 liters per minute. In the case of the G-52 catalyst the effect of increasing the recycle rate is not quite as marked and there is a tendency to level off at the higher recycle rates.

The effect of decreasing the water content of the recycle gas was investigated. In the case of carbonyl iron the reaction rate was more than doubled when the water content of the recycle gas was reduced from the normal 2.8% to zero. In the case of G-52 catalyst, the reaction rate was increased about 30% by reducing the water content of the recycle gas from 3.3% to zero. The difference in the effect of water removal on the reaction rates of the two catalysts is believed due to differences in the reactivity of the catalysts and to the fact that the composition of the recycle gas was different in the two tests.

A preliminary design of a 100 man capacity carbon dioxide reduction system has been made. The system is estimated to have a weight of 455 lbs. and a volume of 31 cu. ft. The power consumption for operating the equipment is estimated at 2.5 Kw. Automatic controls have been devised that will minimize the attention required to operate the equipment. The amount of catalyst that will be consumed is uncertain, but is expected to be entirely acceptable.

It is concluded that the use of a fluidized bed for reacting carbon dioxide and hydrogen to produce carbon and water is entirely feasible. Furthermore, it is believed that at least some of the carbon can be used on board for odor and possibly aerosol control. The carbonyl iron catalyst has shown a reaction rate of up to 350 volumes of reaction gas/vol. of catalyst/hour, corresponding to a volume of 0.66 cu. ft. (96 lb) of catalyst for a 100 man capacity system. The success achieved in the continuous removal of carbon with this system indicates one of the advantages this system shows over other systems.

3.0 SUBMARINE ATMOSPHERE CONTROL

Submarine crewmen continuously consume oxygen and produce carbon dioxide in the process of respiration. When the submarine is sealed, as during and preparatory to diving, there is no access to outside air and the oxygen is depleted and the carbon dioxide concentration is increased. Fresh air contains about 20.9% oxygen and 0.03% carbon dioxide. Persons can endure long time exposure to atmospheres containing as much as 1% carbon dioxide and as little as 17% oxygen without noticeable adverse effects. In a sealed submarine having 700 cu. ft. of atmosphere per crewmen, the uncontrolled concentration of carbon dioxide will reach 1% in 6.5 hours, while that of oxygen will reach 17% after 28 hours. It is thus clear that the carbon dioxide limit will be reached long before the crew begins to suffer from lack of oxygen (Reference 2).

In addition to the primary problems of oxygen and carbon dioxide control, there are problems of temperature, humidity, odor, and aerosol control in submarine atmospheres The work under Contract Nonr 3431(00)(FBM), however, is aimed primarily at the main oxygen and carbon dioxide problems. Other control problems are considered only incidentally in this report.

The older Diesel-Electric submarines did not have a serious atmosphere control problem, because dives were normally limited to a few hours. With the advent of the nuclear powered submarines, the atmosphere control problem became acute because of the capability of almost unlimited underwater operation. The methods that have been used to provide oxygen and to remove carbon dioxide are discussed briefly in the following sections.

3.1 Oxygen Provision

The three main sources that have been used to supply oxygen to submarine crews are storage of elemental oxygen, chemical production of oxygen, and oxygen production by the electrolysis of water.

Some elemental oxygen is usually carried on submarines for emergency purposes. This is normally carried as the compressed gas at a pressure of about 3,000 psi, although liquid oxygen (LOX) has been used to a limited extent. Oxygen can also be carried as a gas under pressure just above the critical temperature (-181.8°F). This type of cryogenic storage is advantageous for use under weightless conditions where there is a problem of separating liquid from gaseous oxygen. There appears to be no particular advantage in this type of cryogenic supercritical storage in submarines.

Oxygen can be generated on submarines by chlorate and perchlorate candles. Such candles consist essentially of mixtures of sodium or lithium chlorates or perchlorates with iron powder. The candles are ignited by heating to about 600°C. At this temperature the chlorate or perchlorate decomposes to the corresponding chloride, giving off oxygen. The iron is oxidized, using up part of the oxygen, but supplying the heat necessary to sustain the high temperature reaction. Chlorate candles are carried on some submarines as stock items.

The bulk of the oxygen supplied to the crews of nuclear powered submarines is supplied by the electrolysis of water to oxygen and hydrogen. Modern electrolysis cells used in submarines operate at 3000 psi so that the hydrogen generated can be vented overboard without the use of a compresser.

3.2 Carbon Dioxide Removal

Carbon dioxide can be removed from the submarine atmosphere by chemical reaction or by physical adsorption on suitable materials. Lithium hydroxide has been widely used for carbon dioxide removal by chemical reaction. The result of this reaction is lithium carbonate which is stored on board, or thrown overboard, since lithium hydroxide cannot be readily recovered from the carbonate. Physical adsorbants include such things as silica gel and molecular sieves, from which the carbon dioxide can be removed by heating to a moderately high temperature or by lowering the pressure.

The method of carbon dioxide removal that is now being widely used in submarines is to absorb the gas in a liquid amine solution, from which it is recovered by a heating and stripping process. The carbon dioxide is held in the amine solution by weak chemical bonds, hence this is considered to be a chemical method. It resembles the physical method, however, in that the carbon dioxide can be recovered and the absorbing amine solution regenerated. Modern nuclear powered submarines use this method of carbon dioxide removal. The carbon dioxide that is recovered is pumped overboard (Reference 2).

3.3 Problems Associated with Atmospheric Control

As indicated in the discussion in the previous sections, the modern nuclear powered submarines are producing oxygen and hydrogen by the electrolysis of water. The oxygen is used to replace that consumed by the respiration of the crew and the hydrogen is vented overboard. Carbon dioxide is removed from the atmosphere and also vented overboard. There are some undesirable aspects of this type of operation. For purposes of discussion these can be divided into engineering and detection problems.

3.3.1 Engineering Problems

The engineering problems associated with venting gases overboard are not severe as long as the depth of operation is not great. However, with increasing depth the problem becomes increasingly difficult. This is due to the fact that the gases must be brought to a pressure greater than that of the ambient water and then venter overboard through one or more openings in the submarine pressure hull.

It was mentioned previously that the hydrogen is now being produced at 3000 psi to avoid the pumping problem. It is not feasible to regenerate the carbon dioxide at high pressure and hence this gas must be compressed by mechanical compressers. It may also become necessary to compress hydrogen before it is rejected if the operating depth of submarines increases to a marked degree. The serious problems associated with compressing gases to pressures of several thousand psi are well recognized.

Another disadvantage of the venting process is the necessity for providing openings in the pressure hull. This becomes more serious as the pressure increases, since special reinforcing of the hull becomes necessary. The possibility of flooding due to equipment failures in lines leading through the pressure hull is a hazard that becomes more serious as the pressure increases.

3.3.2 Detection Problems

The principle mission of the nuclear powered fleet ballistic missile (FBM) submarine is to serve as a deterrent to potential enemies by imposing a retaliatory threat that cannot be neutralized by an initial all-out nuclear attack. In order to serve as such a deterrent it is necessary for the FBM submarine to remain undetected for long periods in waters that are adjacent to, and hence under the nominal control of the potential enemy. It is evident that if the potential enemy were able to detect the presence of the FBM submarines, then they would lose their deterrent function, since they too could be neutralized in the initial all-out attack.

The practice of venting gases overboard may involve detection hazards because of the associated noise and the possibility of the existence of visible gas bubbles. A potentially more serious hazard is due to the change in sea water composition because of the presence of dissolved foreign materials.

3.3.2.1 The Noise Problems

Any venting of gas into liquids results in some noise production. The amount of noise is a function of a number of factors of which an important one is the pressure drop incident to venting. The desirability of venting the hydrogen in small bubbles to facilitate solution tends to make the pressure drop high and hence tends to make the noise problem more severe. Since the submarine may operate at various levels, this necessitates variable venting pressures if the pressure drop is held constant. When venting pure carbon dioxide overboard there is a possibility of cavitation noises owing to the rapid solution of the gas in the water at high pressure. This can be avoided by mixing hydrogen with the carbon dioxide, but this may or may not be readily achieved. In general it would appear that the noise problem can be kept within acceptable limits, but to do this involves some troublesome design and control problems.

3.3.2.2 The Visible Wake Problem

Carbon dioxide is so soluble in sea water that there is little chance of it leaving a visible wake that would be a detection hazard even at shallow depths. Hydrogen, however, is much less soluble and a visible wake is a distinct possibility at shallow depths. This has been recognized and special arrangements have been made to minimize the hazard. The possibility of a visible wake from hydrogen at appreciable depths is usually discounted. However, there is reason to believe that under some conditions this is a distinct possibility.

This might occur under conditions where considerable hydrogen in very small bubbles is injected into quiet, or slowly moving water. Under these conditions the water becomes saturated with hydrogen and small bubbles of gas remain undissolved. The volume of water containing the small bubbles is then lighter than the surrounding water and it rises to the surface as a milky wake that is readily visible. Wakes of this type have been observed when launching torpedoes by air ejection where a device was used to "swallow" the main air bubble. In such cases the main bubble does not rise to the surface, but a milky wake containing fine air bubbles has been observed to rise and form a visible spot.

3.3.2.3 The Change in Sea Water Composition

Any soluble substance that is added to sea water results in a change in composition that is theoretically detectable. In actual practice, however, the degree of detectability varies widely from one substance to another. Thus the addition of small amounts of fresh water would be hard to detect since it would only affect salinity and this has considerable natural variation. However, dissolving foreign gases such as carbon dioxide and hydrogen could involve a serious detection problem.

The detection risk associated with venting carbon dioxide is believed to be much less than is the case with hydrogen. The dissolved carbon dioxide reacts with water to form carbonic acid. This results in a decrease in the pH of sea water which may or may not be readily detectable, depending on the concentration of carbon dioxide in the water. Sea water contains natural buffering materials and this tends to minimize the change in pH. The change in carbonate concentration resulting from the solution of the carbon dioxide is also detectable, but sea water already contains about 0.7% carbonate ion by weight. It is concluded that there is a distinct detection hazard associated with venting carbon dioxide, but there are some formidable obstacles associated with such a detection system.

In the case of hydrogen the detection hazard appears to be much more acute. Molecular hydrogen does not react with any of the constituents of sea water and hence forms a stable solution. Moreover, natural sea water does not contain molecular hydrogen and hence the detection of dissolved molecular hydrogen would be excellent evidence of the presence of a submarine.

The seriousness of the hazard is intensified by the fact that the presence of dissolved molecular hydrogen in sea water is very easy to detect. The gases dissolved in natural sea water consist of oxygen and nitrogen in various proportions. When sea water is subjected to reduced pressure these gases are evolved. If the molecular hydrogen were present it would be evolved also and there would result a gaseous mixture of oxygen, nitrogen and hydrogen. Very small amounts of hydrogen are readily detected in such mixtures because of the great difference in molecular weight and the resulting wide variation in thermal conductivity. It would then be conceptually quite easy to design a device that could be dragged through the water that would continually test for dissolved hydrogen. A number of these at various depths would make it possible to pick up the trail of a submarine and follow it. This would make it possible for a potential enemy to keep FBM submarines under surveillance in times of peace. Under wartime conditions it is therefore possible that the dissolved hydrogen trail of a submarine could be used as a means of surveillance and detection and contribute to its destruction.

It appears that in order to minimize the detection hazard, FBM submarines should have the capability of operating under conditions where no sea water soluble material is vented overboard with the possible exception of water.

4.0 TECHNICAL BACKGROUND OF CARBON DIOXIDE REDUCTION

The discussion of technical background can be conveniently divided into considerations of chemical reactions, catalysts, fluidized catalyst beds, and carbon removal.

4.1 Chemical Reactions

The reduction of carbon dioxide (CO_2) with hydrogen (H_2) to form carbon and water can be represented by the following overall reaction.

$$CO_2 + H_2 \rightarrow C + 2\,H_2O$$

This reaction may take a number of different paths with various intermediate products. Some of the various reactions that may take place are listed below (Reference 4) together with heats of reaction at 25°C.

	Reaction	Δ H KCal/g mole (25°C)
1.	$CO_2 \rightarrow CO + 1/2\ O_2$	+ 67.41
2.	$CO \rightarrow C + 1/2\ O_2$	+ 26.62
3.	$CO_2 \rightarrow C + O_2$	+ 94.03
4.	$CO_2 + H_2 \rightarrow CO + H_2O$	+ 9.65
5.	$2\ CO \rightarrow C + CO_2$	- 40.79
6.	$C + 2\ H_2 \rightarrow CH_4$	- 17.87
7.	$CO + H_2 \rightarrow C + H_2O$	- 31.14

Bearing in mind that reactions with high positive Δ H values do not take place to any extent, it is evident that reactions 1, 2, and 3 above are of no interest at 25°C. Reference 4 also gives equilibrium values at higher temperatures and in general, these three reactions do not go appreciably up to 2000°F. We are therefore primarily interested in reactions 4, 5, 6, and 7. Reaction 6, leading to the formation of methane, is an undesirable side reaction which we would like to minimize, or reverse. It is of interest to examine the effect of temperature on the equilibrium values of these four reactions.

The logarithms of the K_p values at various temperatures are listed in Reference 4 and shown graphically in Figure 4-1. The K_p values are a measure of the equilibrium composition of the product and reaction gases. In general, if x moles of A react with y moles of B to produce z moles of C and r moles of D, then

EQUILIBRIUM CONSTANTS VERSUS TEMPERATURE FOR REACTIONS OF INTEREST

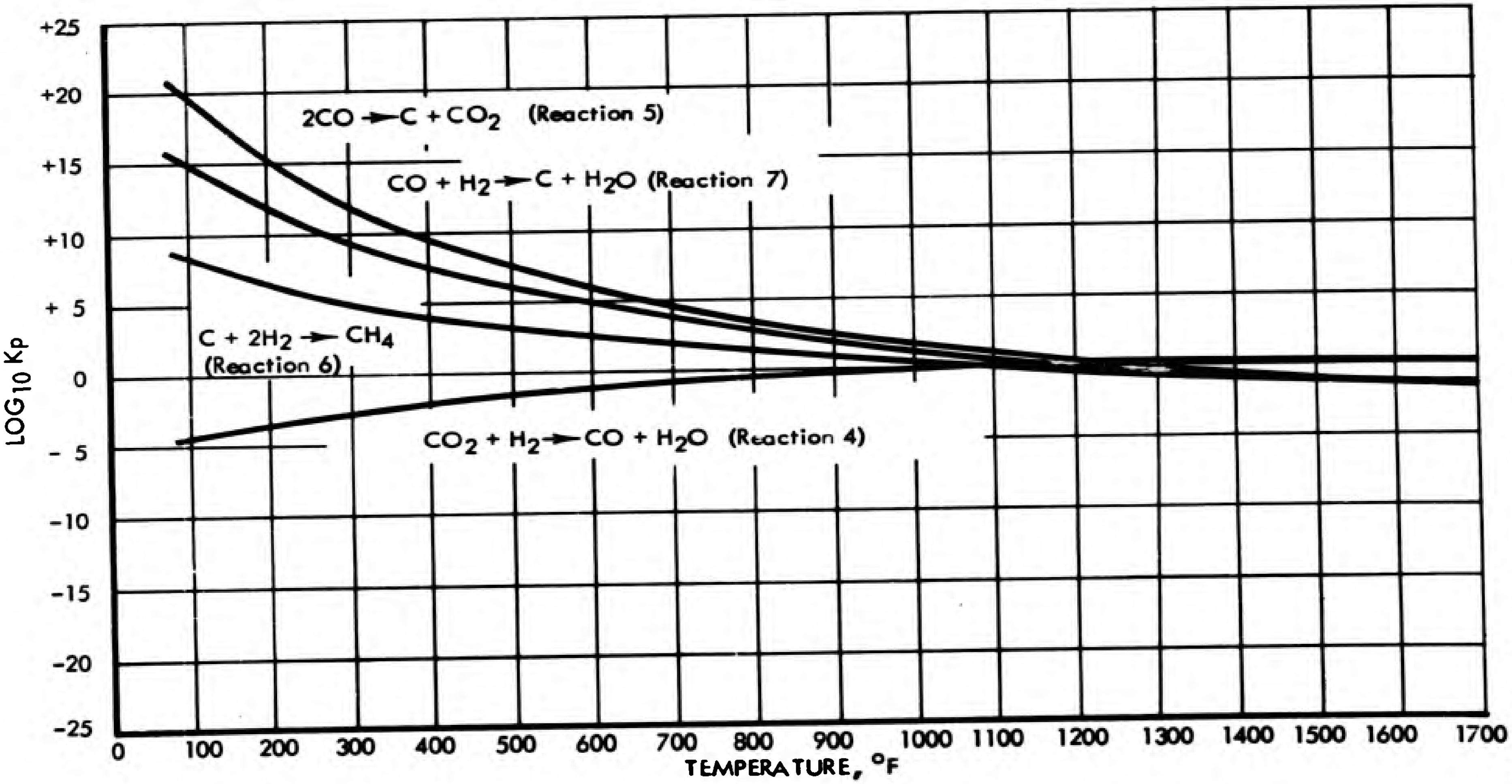


FIGURE 4-1

$$K_p = \frac{P_C^{\ z}\ P_D^{\ r}}{P_A^{\ x}\ P_B^{\ y}}$$

where $P_C^{\ z}$ etc. is the partial pressure of component C raised to the power z. If K_p has a large positive value (log K_p is large and positive) then the reaction goes far toward completion. Whereas if K_p is very small (log K_p is large and negative) then the reaction does not go appreciably, even if equilibrium is achieved. If K_p is in the vicinity of 1 (log K_p = 0) then the reaction goes partly and can be driven one way or the other by varying the partial pressure of the reactants and products.

An examination of Figure 4-1 shows that, in general, the equilibrium picture is better at the lower temperatures. Reaction 4, commonly called the water gas shift reaction, has an unfavorable K_p at low temperatures, but it is not highly unfavorable and can be driven in the right direction by removing water. Likewise reaction 6, a side reaction that produces methane, has a positive value at low temperatures. However, here again, it is not highly positive.

While the equilibrium considerations favor low temperature operation of the process, it is difficult to approach equilibrium under these conditions. Hence, it would appear desirable to operate at the lowest temperature at which a good reaction rate can be maintained.

4.2 Catalysts

In order to approach equilibrium conditions at low temperatures in carrying out the desirable reactions 4, 5, and 7 from Figure 4-1, a catalyst is required. Iron has long been recognized as a desirable catalyst for the purpose (Reference 1, 3, 5, 6). Other catalysts that have been shown to have activity in promoting reactions of this kind are nickel, cobalt, and copper (Reference 6).

Most of the work in this area has been done with iron catalysts. The best results have been obtained when the iron has a large surface area. In the process of the reaction the iron appears to be consumed. This results from the formation of iron carbide, which is an undesirable side reaction. Literature reports on the reaction of carbon monoxide and hydrogen to produce carbon and water show that up to 120 grams of carbon can be formed by one gram of iron (Reference 3). Iron, nickel, and cobalt all form the catalytically inactive carbide under the conditions of reaction. The higher temperatures favor the formation of the carbide, (Reference 3). Data on the free energies of the reactions leading to the formation of the iron carbides cementite (Fe_3C) and Hagg carbide (Fe_2C) indicate that high temperatures favor the reaction of iron with carbon, while low temperatures favor the reaction of iron with carbon monoxide. These data are presented below (Reference 7).

FREE ENERGIES OF REACTION LEADING TO IRON CARBIDE FORMATION

ΔF in K Cal for Reactions Noted

T,°F	T,°C	$3 Fe + C = Fe_3C$	$2 Fe + C = Fe_2C$	$3 Fe + 2 CO = Fe_3C + CO_2$	$2 Fe + 2 CO = Fe_2C + CO_2$
32	0	+4.487			
250.6	127	+4.043			
350.6	177		+3.866		
450.6	227	+3.461	+3.821	-16.6	-16.2
620.6	327	+2.82	+3.458	-12.9	-12.3
710.6	377		+3.140		
800.6	427	+2.16			

Since iron carbide formation is reported to be less severe at low temperatures, it is presumed that the reaction with carbon monoxide does not approach equilibrium under the conditions usually used for carbon dioxide reduction.

Iron catalyst can be poisoned by sulfur compounds, as well as by cyanide and ammonia. Water has also been reported to be a retardant to the carbon-forming reactions, but this is apparently a mass action effect tending to reverse reaction 3 of Figure 4-1.

4.3 Fluidized Catalyst Beds

The technical background of fluidized catalyst beds is summarized in Reference 9. In brief, such a bed consists of a layer of finely divided catalyst particles. At the bottom of the bed the fluid undergoing reaction is introduced in such a way that it is evenly distributed over the area of the bed. The fluid then passes up through the bed and the process of fluidization may be described as follows (Reference 9).

(1) At low fluid velocities the particles remain static and the pressure drop increases with velocity in the normal way.

(2) With increasing velocity a critical point is reached where the pressure drop corresponds to the buoyed weight of the bed, the particles are lifted out of contact with each other, and the bed as a whole begins to expand.

(3) Upon further velocity increase, the pressure drop remains substantially constant but bed expansion continues. If the fluid is gaseous, bubbles form and rise through the bed and the behavior is much like that of a boiling liquid.

(4) At high volocities, the free surface disappears and particles are continuously transported from the vessel and the pressure drop keeps increasing with the volocity. This stage of fluidization corresponds to the gaseous state. It is often called dilute-phase fluidization, in contrast with dense-phase that exists when an observable free surface exists.

When applied to the reduction of carbon dioxide with hydrogen to carbon and water, the fluidized catalyst bed would be expected to have the following advantages (Reference 9).

(1) In a fluid bed a far greater surface area can be exposed to a gas by the use of smaller particles than is possible in a fixed bed where a lower limit of particle size is fixed by an upper limit of allowable pressure drop. This is possible since the pressure loss theough a uniformly fluidized bed is essentially a function of bed height and particle density and is independent of particle size.

(2) A corollary to the first advantage is that high reaction rates are possible in fluidized systems involving solid-gas interaction as is the case for CO_2 reduction in the presence of a catalyst. Thus the use of a fluidized bed permits a reduction in reactor volume.

(3) The violent motion of the particles and collisions among the particles leads to gradual attrition of the particle surface. This fact, which is generally a disadvantage in most cases, is to be used advantageously in this application since carbon will be formed at the particle surface and needs to be knocked off to maintain high rates and also remove it

from the bed. Detaching the carbon from the particles should not be a problem as our observations on steel wool have indicated it is loose and weakly attached.

(4) The violent motion of the particles tend to homogenize all intensive properties of the bed. There is a constant top-to-bottom turnover of the bed. This is beneficial in this application not only because the carbon will be depositing uniformly throughout the entire catalyst volume, but also because it becomes easier to transport the carbon deposited at the bottom of the reactor to the top, into the gas phase and out.

(5) This circulation and violent motion of the particles also promotes uniform temperatures in the bed and high heat transfer rates in or out of the bed.

(6) Fluidized solids behave in a manner similar to liquids and can be readily transported in or out of a fluid bed as well as from one vessel to another. Thus it is possible when necessary to add or remove solids from a system.

(7) Since the properties of a preperly operating bed will be uniform with respect to both time and position the performance should be easier to maintain constant, and catalyst system differences simpler to distinguish.

A wide variety of catalyst particle sizes has been used in fluidized beds. In general the particles should be small to increase surface area, but not so small that the material does not flow readily. Screen sizes of 20 to 200 mesh (840 to 74 microns) have been widely used (Reference 9).

In designing reactors using fluidized catalyst beds wide ranges of bed height to area ratio may be used (Reference 10). The height of bed should be sufficient to obtain the desired amount of contact with the catalyst and this depends on catalyst activity, equilibrium considerations, etc. For beds having a large area to height ratio, it is important to have the incoming fluid evenly distributed over the bottom of the bed. This may be done by providing multiple fluid inlet orifices and taking an appreciable pressure drop through each orifice. The amount of pressure drop required to obtain good bed performance varies from case to case. A good rule to follow is to make the pressure drop at least as large as the normal fluctuations in pressure drop through the bed (Reference 10, p. 224).

4.4 Carbon Removal

In reactions where carbon dioxide and hydrogen are fed into a fixed bed of catalyst, the carbon formed tends to accumulate in the interstices of the catalyst and eventually chokes the bed. The time required to choke the bed varies widely with conditions, but has been reported as one to two days by two investigations (References 5 and 6). Removal of carbon from fixed beds by violent agitation or blow-down has not been shown to be feasible (References 6 and 8).

The possibility of using a fluidized catalyst bed instead of a fixed bed was suggested by Reference 9. The fact that the bed is in continuous motion due to the reaction gases passing through the bed means that the carbon can be continuously carried from the bed and removed from the system by suitable means. This is the method of carbon removal that has been investigated during the work now being reported.

5.0 EXPERIMENTAL APPARATUS

The contract specified an experimental system that would be capable of consuming 0.14 pounds of CO_2 per hour. The experimental apparatus used in this work was designed to meet these requirements. In actuality, the apparatus has far exceeded this requirement with an active catalyst under good operating conditions.

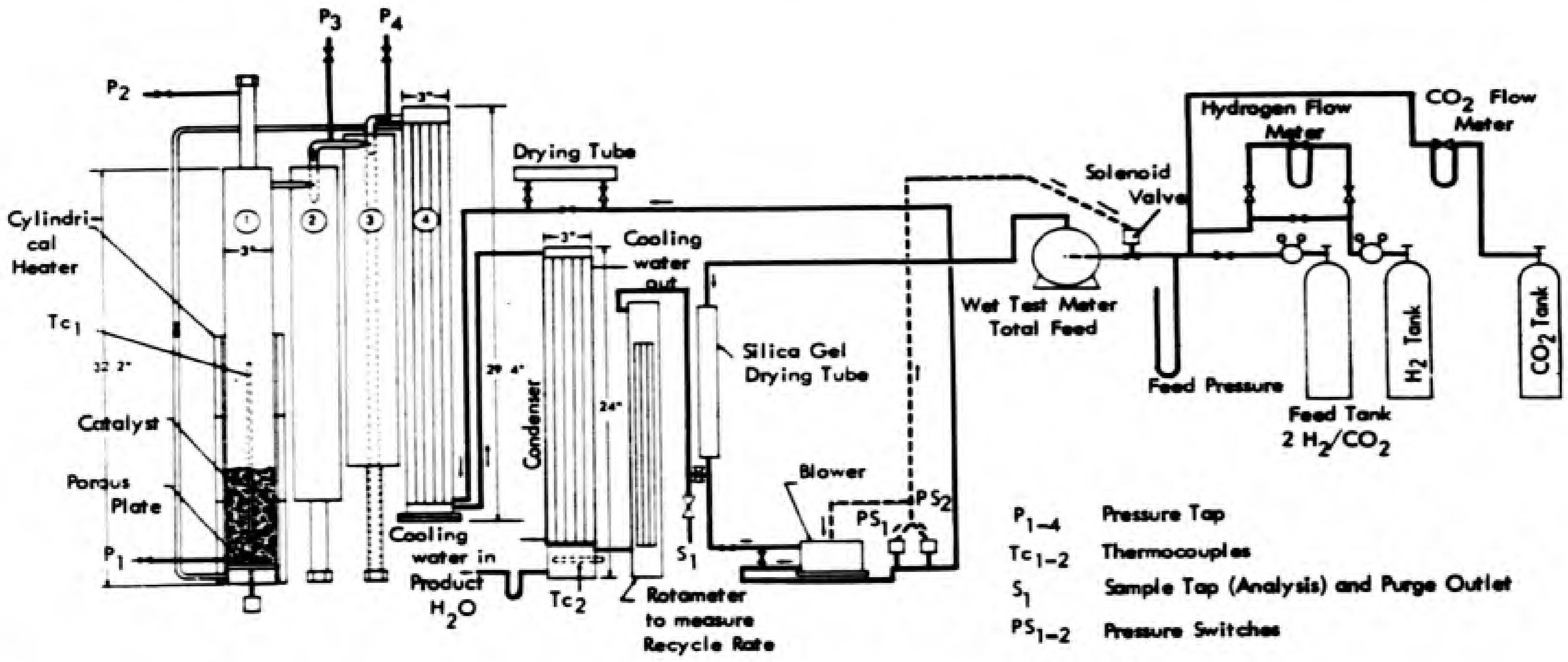
A flow sheet of the apparatus used is shown in Figure 5-1. The various parts of the equipment may be described briefly as follows. The reactor consists of a type 304 stainless steel tube 3" I.D. heated by external electric heaters. It has a porous plate welded near the bottom. This is 3/32" thick and is made of type 316 stainless steel. The average pore size is 165 microns. The powdered or granulated catalyst rests on this plate and is kept in a fluidized state by reaction gas that passes up through the porous plate. The reaction gas, carrying the carbon and water resulting from the reaction, passes into the cyclone separator where the carbon is separated. It then passes into a filter where any remaining carbon is separated. It next goes through a heat exchanger where it gives up most of its sensible heat to the recycle gas on its way to the reactor.

The heat exchanger consists of a 3" stainless steel tube with headers in each end supporting a tube bundle consisting of 55 stainless steel tubes each 0.25" O.D. with a 0.028" wall and a length of 27.5". The reaction gas leaving the reactor passes through the tubes, while that returning to the reactor passes through the shell. The shell area has 8 baffles interspersed along the length of the tube bundle to make the shell gas pass back and forth across the tubes.

On leaving the heat exchanger, the cooled gas next passes into a water-cooled condenser where it is cooled still further and the water vapor is partly condensed, leaving only an amount which approximately corresponds to the saturated vapor pressure at the temperature of the cooling water. The condenser consists of a 3" stainless steel tube with headers in each end supporting a tube bundle that is identical to that used on the heat exchanger except that it is 19" long and has seven baffles. The cooling water flows through the shell, while the reaction gas flows through the tubes. Water collects in the bottom of the condenser below the tube header and is drawn off as desired.

The gas next passes through a rotameter to measure the recycle rate. On leaving the rotameter, the gas next goes to the recycle pump or blower. A diaphragm-type

FLOW SHEET - CO_2 REDUCTION EXPERIMENTAL EQUIPMENT



P_{1-4}	Pressure Tap
Tc_{1-2}	Thermocouples
S_1	Sample Tap (Analysis) and Purge Outlet
PS_{1-2}	Pressure Switches

UNIT NO.	FUNCTION	
1	Fluidized Reactor	
2	Cyclone Separator	Carbon Accumulators
3	Filter	
4	Heat Exchanger	

UNITS 1, 2, 3, 4 WELDED TOGETHER AS A UNIT AND INSULATED BY WRAPPING WITH KAOWOOL

FIGURE 5-1

paint spray compressor is now being used for this purpose. This pump has a neoprene diaphragm and is not considered to be entirely satisfactory because under continuous operation the diaphragm has a life of only about one week. A blower is considered to be the ideal solution to this problem, but a blower for the experimental apparatus that is suitable in all respects has not been found. Attempts to use an oil-sealed vane-type pump were unsuccessful because of oil contamination of the recycle gas.

The gas next passes back through the heat exchanger to the reactor. In order to determine the effect of moisture on the reaction rate, a drying tube can be inserted in the line between the rotameter and the heat exchanger.

Fresh feed is added to the recycle gas between the rotameter and blower. This is passed through a wet test meter and then dried to prevent the introduction of water with the feed. The feed is supplied from compressed gas cylinders filled with a mixture of approximately two moles of hydrogen to one of carbon dioxide. A hydrogen tube is connected into the system for the purpose of supplying hydrogen for the pretreatment of catalyst. Since the feed gas as received may be slightly deficient in either hydrogen or carbon dioxide, provision is made to add additional amounts of either of these gases.

6.0 EXPERIMENTAL PROCEDURE

The procedure used in making a run on the apparatus may be described briefly as follows. The apparatus is cleaned out as thoroughly as possible from the previous run and a new filter matt installed in the filter. The catalyst is next introduced and the apparatus closed, assembled, and tested for leaks, under about 16' of mercury pressure using helium as the pressurizing gas. When demonstrated to be free from leaks, the apparatus is purged with about 33 liters of hydrogen (the apparatus has a volume of about 11 liters). The recycle pump is operated during purging and the purge rate is never more than half the recycle rate.

The heat is now turned on and the temperature brought up to 800°F, feeding hydrogen to maintain about 1" Hg positive pressure on the feed pressure manometer. The apparatus is run at 800°F until the hydrogen feed rate drops substantially to zero, at which point it is assumed that the catalyst is completely reduced. About twelve liters of feed gas is now purged into the apparatus and operation continued until the reaction rate levels off. The temperature is then increased to 850°F and operation continued at that temperature until the feed rate levels off. This process is repeated until the desired operating temperature is reached.

Readings are normally taken every 15 minutes. These normally include noting the time, feed meter reading, feed pressure, feed rate since the last reading, recycle rate, bed pressure drop, reactor temperature, condenser cooling water temperature and water formed since the last reading or last water withdrawal.

Analyses of the recycle gas are made as desired, using a Beckman chromatograph. This apparatus does not give a good indication of hydrogen content if the concentration is above about 35%. In such cases the hydrogen concentration is determined by difference.

During the run, the feed gas is supplemented by hydrogen or carbon dioxide to adjust the recycle gas to desired compositions. If such desired changes are radical in nature, the feed gas may be discontinued temporarily and pure hydrogen or carbon dioxide fed until the desired composition is obtained. In some cases when the feed rate is quite low, owing to the recycle gas composition being hydrogen rich or carbon dioxide rich, some of the recycle gas is purged to save time in obtaining the desired corrections. All purging reported in the runs is for this reason, or in a few cases to reduce the high nitrogen content of the recycle gas that has resulted from a leak at the pump inlet where the pressure is below atmospheric.

At the end of the run the apparatus is cooled and disassembled. The contents of the reactor, cyclone separator, and filter are removed, weighed and analyzed for carbon content. These materials were also analyzed for hydrogen until it was established that the hydrogen content was always negligible.

7.0 EXPERIMENTAL RESULTS

Using the apparatus shown in Figure 5-1, a number of experiments have been carried out. These tests have been designed to test various catalysts for this application and to determine the effect of the various controllable operating parameters on the reaction rate.

7.1 Tests on Various Catalysts

The significant experiments carried out to test various catalysts are summarized in Table 7-1. It will be noted that tests have been carried out on G-52 catalyst (nickel supported on a refractory oxide), commercial iron powder, nickel powder, type 304 stainless steel powder, sponge iron (reduced iron oxide) powder and carbonyl iron powder. The reaction rates quoted in Table 7-1 are nominal values obtained on feed gas containing about 66% hydrogen and 34% carbon dioxide. Much higher reaction rates can be obtained by varying the feed composition, as shown by the parametric studies reported in Section 7.2.

7.1.1 G-52 Catalyst

Two tests, runs 4 and 14, were made on G-52 catalyst. This is a very active material having good life characteristics. However, the catalyst is so light that it is difficult to separate from the carbon. It will be noted that during run 14 more than half the catalyst was carried out of the reactor during the run. The catalyst is made of very finely divided material that is formed into pellets. The material used in runs 4 and 14 was made by breaking up these pellets and screening to the desired size. It appears that during the run, these granules break into very fine particles that are carried over with the carbon. While it may be possible to get around this difficulty, the solution to the problem is not clear at present. It is interesting to note that the catalyst was still highly active at the end of run 14 after 102 hours. There was no carbon sticking to the walls of the reactor after the run. The catalyst was still highly fluid.

7.1.2 Commercial Iron Catalyst

This is an iron powder commonly used in powdered metallurgy applications. It was supplied by the Easton Metal Powder Company who supplied the following typical analysis.

TABLE 7-1
SUMMARY OF DATA ON RUNS 4 THROUGH 19 – REDUCTION OF CO_2

RUN NO.		4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Catalyst		G-52	Commercial Iron Powder	Nickel Powder	Stainless Steel	Sponge Iron	Commercial Iron	Commercial Iron	Commercial Iron	Commercial Iron	Commercial Iron	G-52	99% Carbonyl Iron 1% G-52	99% Commercial Iron 1% G-52	99% Commercial Iron 1% G-52	99% Carbonyl Iron 1% G-52	99% Carbonyl Iron 1% G-52
Sieve Size		30-325	100-200	100-200	100-200	80-200	100-325	100-200	100-200	100-200	100-200	30-325	100-200 30-325	100-200 30-325	100-300 30-325	100-200 30-325	100-200 30-325
Wt. Catalyst Charged (g.)		515.6	1400	1868.5	1204.9	1593.15	1394.9	1400	1400	1400	1400	485.8	1203 12	1382 14	1417 14	1237.4 13	639.1 6.4
Vol. Catalyst Charged (ml.)			540	520	520	520	520	530	518	530	530	520	520 12.8	520 15	520 15	520 13.9	260 6.9
Total Liters Fed During Run		975.64	543.00	4.04	30.59	12.70	55.3	48.3	50.0	56.48	59.84	1806.58	1615.47	78	169	1661.11	2859.8
Liters Purged		94	105		64		42	42	42.8	42.8	42.3	96.12	63	42	60		26
Net Liters of Feed		881.64	438	4	24.6	12.7	13.3	6.3	7.2	13.68	17.54	1710.46	1552.47	36	109	1661.11	2833.8
Reaction rate ml./min at	800°F		2	0	0	6	2	3	1	2	1	150	23		6		
	900°F		43	3	8	18	12		1	11		400	100		12	220	160
	1000°F	300	165		30	80	28		9			500	280	16	24		450
	1100°F		330		25	100							1100	64	76	1150	950
	1200°F		350		13							1000			174		
Fluidization of Catalyst Bed		OK	OK	Failed at 900°F	OK	Failed at 1100°F	Failed at 1000°F	Failed at 820°F	Failed at 1000°F	Failed at 900°F	Failed at 850°F	OK	OK	Failed at 1175°F	Failed at 1220°F	OK	OK
Reactor Content After Run (g.)		541.95	1430.8	1889.5	1207.75	1560.85		1378.55	1355.24			306.0	1405			1585	948.5
Carbon on Catalyst (%)		19.75	4.84	0.21								49.1	17			18.5	37.1
Wt. Carbon in Reactor (g.)		107.0	67.8									151.0	239			294	352
Separator Content After Run (g.)		21.3	15.9	4.1		20.1		5.1	8.4			323.5	37.9			31.3	86.2
Carbon in Separator Content (%)		23.43	15.24 *	14.9								31.3	23.5			25.2	40.1
Carbon in Separator (g.)		5.00	1.1	0.6								101.3	8.9			7.9	34.5
Filter Content After Run (g.)		5.1	2.4									59.7	14.8			9.9	48.0
Carbon in Filter Content (%)		10.96										44.1	46.4			26.5	71.3
Carbon in Filter (wt.)		.56										26.3	6.9			2.6	34.2
Total Carbon Account for (g.)		112.56	68.4									278.6	269.4			304.5	426.3
Carbon Accounted for (%)		77.0	86.9									101.6	112.5			102.5	92.3
Water Collected (g.)		433.6	238.7	4.0	14.0	10.3						806	731			748	1393.5
% Hydrogen Accounted for as Water		98.5	102.0										99.8			97	100.7
% Oxygen Accounted for as Water												98.0	95.8			97	100.7
Cost of Catalyst ($/Lb.)		2.55	0.21	1.64	1.25	0.20	0.21	0.21	0.21	0.21	0.21	2.55	1.77	0.21		1.77	1.77
Duration of Run, Hrs.		112	80	16	7	8	4	1	4	3	11	101	72	5	24	34	82

Fe	98.7%
C	0.06%
Mn	0.15%
Si	0.05%
S	0.022%
P	0.011%
Hydrogen loss	0.65%

Runs 5, 9, 10, 11, 12, 13, 16 and 17 were made on this material. Excellent results were obtained with run 5. The results were considered to be particularly promising because there was good separation of the carbon from the catalyst. While this catalyst is less active than the G-52 catalyst, its activity is considered to be acceptable. With a nominal reaction rate of 330 ml/min of reaction gas (66.7% H_2 and 33.3% CO_2) for 540 ml of catalyst, a volume of 6.6 cu ft of catalyst would be required for a 100 man crew.

After run 5, the iron powder appeared to be free of carbon deposits. Most of the carbon was deposited on the reactor wall above the catalyst bed, much like a soot deposit in a flue. Thus satisfactory separation of the carbon from the catalyst was achieved. While the carbon was not in the separator, where it was expected to be, this was considered to be relatively unimportant, since it was carried out of the catalyst bed and could certainly be removed by suitable arrangements.

One attractive feature of the commercial iron catalyst is its low cost. Table 7-1 lists the cost at $0.21/lb, but this is the price in small lots. For large volume, the price is $0.11/lb.

In run 5 excellent catalyst fluidization was obtained up to temperatures of 1250°F. However, in runs 9, 10, 11, 12, and 13, the catalyst ceased to act as a fluidized bed at temperatures between 820 and 1000°F. In all cases the iron powder was caked. At first it was believed that these difficulties were due to contamination of the catalyst bed with oil from the oil-sealed pump that was being used at the time. However, repeat tests with the diaphragm pump and a thoroughly cleaned out reactor gave the same result.

It is now concluded that the excellent result obtained with run 5 was due to traces of G-52 catalyst that were left in the reactor from the previous run.

Iron powder is known to become sticky at about 900°F if it is clean and the surface is reduced. It appears that after carbon starts to form, it coats the iron powder sufficiently to prevent sticking. However, the pure iron is not active enough to produce appreciable carbon at temperatures below 1000°F; hence the pure iron cakes under these conditions. The traces of G-52 catalyst tend to protect the iron, either by coating, or by promoting carbon formation at lower temperatures.

Runs 16 and 17 were next made in an effort to check the good results obtained in run 5. In these runs, 1% G-52 catalyst was added to the commercial iron. The reaction rate was disappointingly low and eventual loss of catalyst fluidization was experienced at around 1200°F. This loss of fluidization is attributed to lack of carbon formation resulting from low catalyst activity and to a too rapid increase in reaction temperature. The low reaction rate obtained in runs 16 and 17 is unexplained. For runs 5, 16 and 17, the iron powder was designated RZ-365 from the Easton Metal Powder Company, Easton, Pennsylvania. The iron powder used in run 5 was from a 5 pound sample, while that used in runs 16 and 17 was from a 100 pound lot purchased at a later date. There is a possibility that the difference in performance was due to differences in the two lots of iron powder. This matter was not pursued further because the carbonyl iron powder tested in the mean time was found to be much more active than any of the other iron powders tested.

7.1.3 Carbonyl Iron Catalyst

This material was supplied by General Analine and Film Corporation. It is made by the thermal decomposition of iron pentacarbonyl ($Fe(CO)_5$). In the process the iron forms extremely fine spherical particles which agglomerate together to form a cake. This is broken up into granules that may be screened to any desired particle size distribution. This results in an iron powder that has a very high surface area and hence is extremely active. This material is currently commercially available in quantities up to 20,000 lb/month. The price in 5 lb lots is $1.77/lb as quoted in Table 7-1. In ton lots the price is $1.47/lb.

The particular powder used in this work was the Grade L. The manufacturer reports that this material has the following characteristics.

Average particle diameter based on weight (microns)		20
Particle density (g/ml)		7.8
Apparent (Bulk) density (g/ml)		1.8 to 3.0
Composition - weight %	Fe (Min)	99.5
"	C (Max)	0.05
"	O (Max)	0.30
"	Ni (Max)	0.05

Runs 15, 18 and 19 were made on this material. The results are summarized in Table 7-1. In all of these runs, the carbonyl iron catalyst showed excellent activity. In each case the catalyst was pyrophoric after the run, indicating an extremely active surface condition. Good fluidization of the catalyst was obtained throughout the runs.

Runs 15 and 19 were terminated because of a high pressure drop through the porous plate used to support the catalyst and distribute the gases across the catalyst bed. The reason for this stoppage is not clear but is believed due to the formation of iron carbonyl during operation on carbon monoxide rich recycle gas. No trouble was experienced with plate plugging during run 18 where operation under these conditions was avoided. The problem of plate plugging is not considered serious because a porous plate will probably not be used in full scale equipment. In addition, the optimum operating conditions are not in the CO rich area of recycle gas composition.

Run 18 was terminated because of an accidental leak that developed in the water withdrawal system. This happened during the night when the equipment was unattended and resulted in exhausting the feed supply and eventual air entry into the system. The hydrogen balance for this run was based on the water collected up to the time of the last reading. An additional 170 g of water accumulated after the last reading, indicating considerable more reaction. However, the carbon balance is unexpectedly good, indicating that some of the expected excess carbon was burned by the air that entered the system.

Run 19 was made with half the usual volume of carbonyl iron catalyst. This was done in an effort to obtain a higher carbon to catalyst ratio in a reasonable time. An effort was made to operate under conditions where a high feed rate would be maintained. However, controls were inadequate for maintaining the desired recycle gas composition overnight and the composition always went hydrogen rich or carbon dioxide rich during the night. However, an average reaction rate of 576 ml/min (133 vol/vol cat/hr) was realized. It is interesting to note that the reaction rate with 260 ml of carbonyl iron catalyst is virtually equivalent to that with 520 ml of catalyst. This indicates that in both cases the gases are being brought virtually to equilibrium composition on each pass. It also suggests the possibility that still less catalyst would suffice. However, the peak reaction rates obtained in this run are such that the volume of catalyst required for a 100 man submarine crew would be 0.66 cu ft. Since this is negligibly small compared to the volume that must be provided in the reactor for disentrainment, etc., there does not appear to be much advantage in using smaller amounts of catalyst.

The distribution of the carbon is of particular interest in run 19. The overall ratio of carbon to catalyst in this run was 0.66, as compared to a ratio of 0.24 for run 18. In run 18 96.5% of the carbon remained with the catalyst. In run 19 this was reduced to 82.5%. It appears that the catalyst at first retains most of the carbon, probably in the interstices in the catalyst granules. However, as the amount of carbon increases, more of it is carried out of the catalyst bed. It would be necessary to run to still higher ratios of carbon to catalyst to determine the equilibrium carbon content where carbon ceased to accumulate in the catalyst bed. Run 19 was terminated as was run 15 because of high pressure drop through the porous plate that supports the catalyst and distributes the incoming reaction gases. This stoppage is attributed to inadvertent operation on carbon monoxide rich recycle gas.

7.2 Parametric Studies

Three catalysts have shown sufficient promise to justify obtaining parametric data. These are the commercial iron powder, the G-52 catalyst and the carbonyl iron powder.

7.2.1 Commercial Iron Powder

The effect of temperature on the reaction rate of commercial iron powder has been investigated. These results, obtained during run 5, are presented in Table 7-2 and are shown graphically in Figure 7-1.

TABLE 7-2

THE EFFECT OF TEMPERATURE ON THE REACTION RATE OF COMMERCIAL IRON CATALYST

(Recycle Rate = 6.7 liters/min.; Condenser Water Temperature = 74°F; Reaction Gas = 2 moles of H_2/mole of CO_2)

Reactor Temperature (°F)	Nominal Reaction Rate Ml/min. for 540 ml. catalyst	 Vol. Reaction Gas/ Vol. Catalyst/Hr.
800	2	0.2
850	17	1.9
900	43	4.8
950	80	8.9
1000	165	18.3
1050	222	24.7
1100	333	37.0
1150	300	33.3
1200	350	38.9
1250	330	36.7

THE EFFECT OF TEMPERATURE ON THE REACTION RATE
OF COMMERCIAL IRON CATALYST

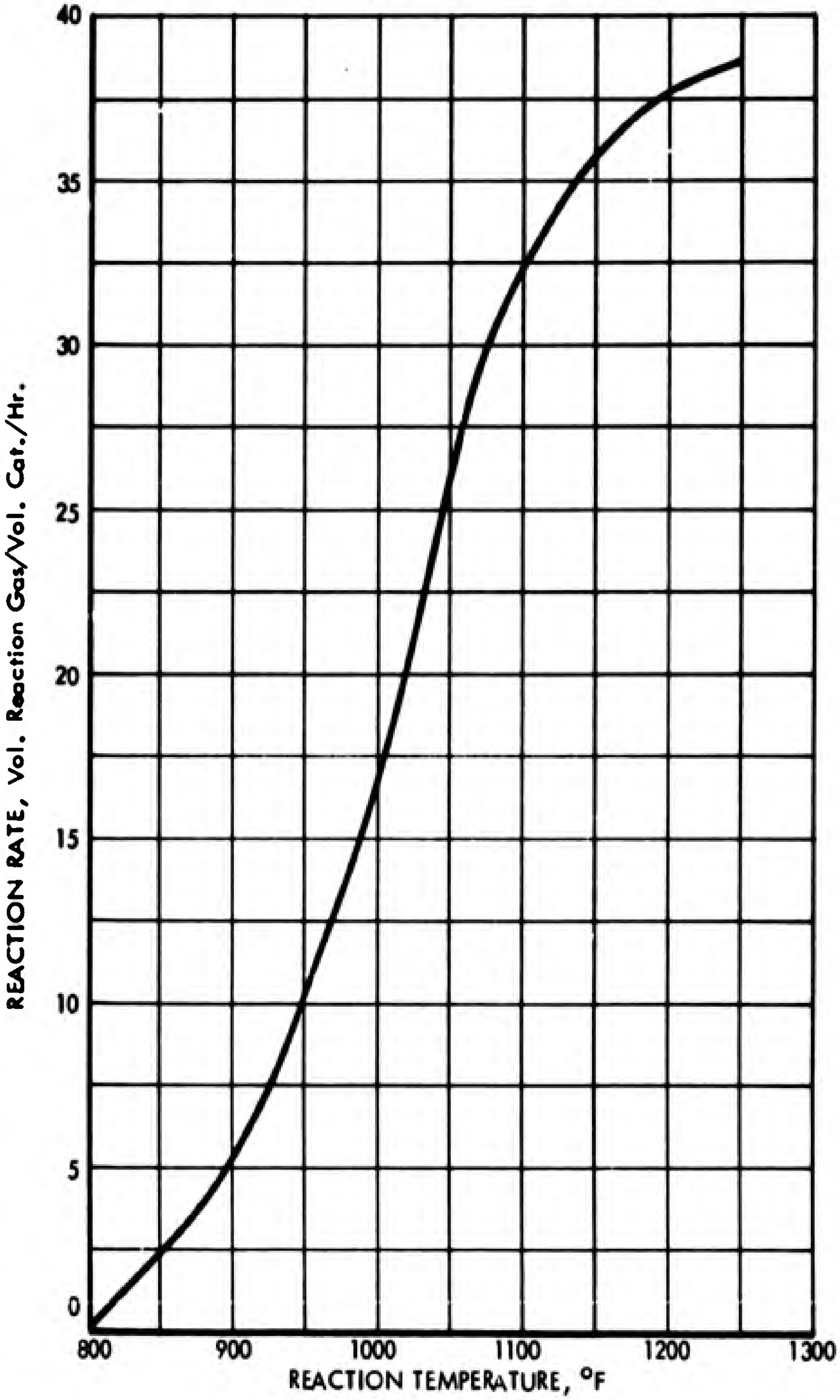


FIGURE 7-1

The shape of the temperature versus reaction rate curve shown in Figure 7-1 is of interest. Up to about 1050°F the curve has the typical exponential shape that is indicative of the effect of increasing temperature on reaction rate. Beyond this point the effect of a less favorable equilibrium situation begins to be felt and the curve begins to flatten off. This is in accordance with the curves shown in Figure 4-1, where it will be observed that the carbon-forming reactions Nos. 5 and 7 show negative $\log_{10} K_p$ values beyond about 1250°F.

7.2.2 G-52 Catalyst

A fairly comprehensive parametric investigation of the G-52 catalyst was made during run 15. The parameters investigated were (1) the effect of temperature, (2) the composition of the recycle gas, (3) the effect of recycle rate, and (4) the effect of water content of the recycle gas on the reaction rate.

7.2.2.1 The Effect of Temperature on the Reaction Rate of G-52 Catalyst

The effect of temperature on the reaction rate of G-52 catalyst at various recycle gas compositions is shown by the studies on the composition of the recycle gas. However, it is of interest to look at the temperature effect on the same basis as that shown for the commercial iron powder catalyst in Table 7-2 and Figure 7-1. Corresponding data on the G-52 catalyst are presented in Table 7-3 and Figure 7-2. It is evident that the reaction rate versus temperature curve shown in Figure 7-2 for the G-52 catalyst is similar to that shown in Figure 7-1 for the commercial iron catalyst, except for the higher reaction rates in the former.

7.2.2.2 The Effect of Recycle Gas Composition on the Reaction Rate of G-52 Catalyst

During run 14, data were obtained on the effect of recycle gas composition on reaction rate at temperatures of 800, 1000, and 1200°F. The feed gas used during the run consisted of 65.8% hydrogen and 34.2% carbon dioxide. Since it was slightly carbon dioxide rich, low ratios of hydrogen to carbon dioxide could be obtained by operating continuously on feed gas. To investigate the effect of high hydrogen to carbon dioxide ratios, hydrogen was added either alone or in addition to the feed gas. Simultaneous gas analyses and reaction rate data were obtained after the apparatus had a chance to equilibrate by operating for about 15 minutes under each set of conditions. The feed rate and analytical data are presented in Tables 7-4, 7-5, and 7-6 for temperatures of 800, 1000, and 1200°F, respectively.

TABLE 7-3

THE EFFECT OF TEMPERATURE ON THE REACTION RATE OF G-52 CATALYST

(Recycle Rate = 6.7 liters/hr.; Condenser Water Temperature = 71°F; Reaction Gas = 2 moles of H_2/mole CO_2)

Reactor Temperature (°F)	Nominal Reaction Rate Ml/min for 540 ml. catalyst	 Vol. Reaction Gas/ Vol. Catalyst/Hr.
800	160	18.5
900	366	42.3
1000	1250	144.2
1200	1625	187.7

THE EFFECT OF TEMPERATURE ON THE REACTION RATE OF G-52 CATALYST

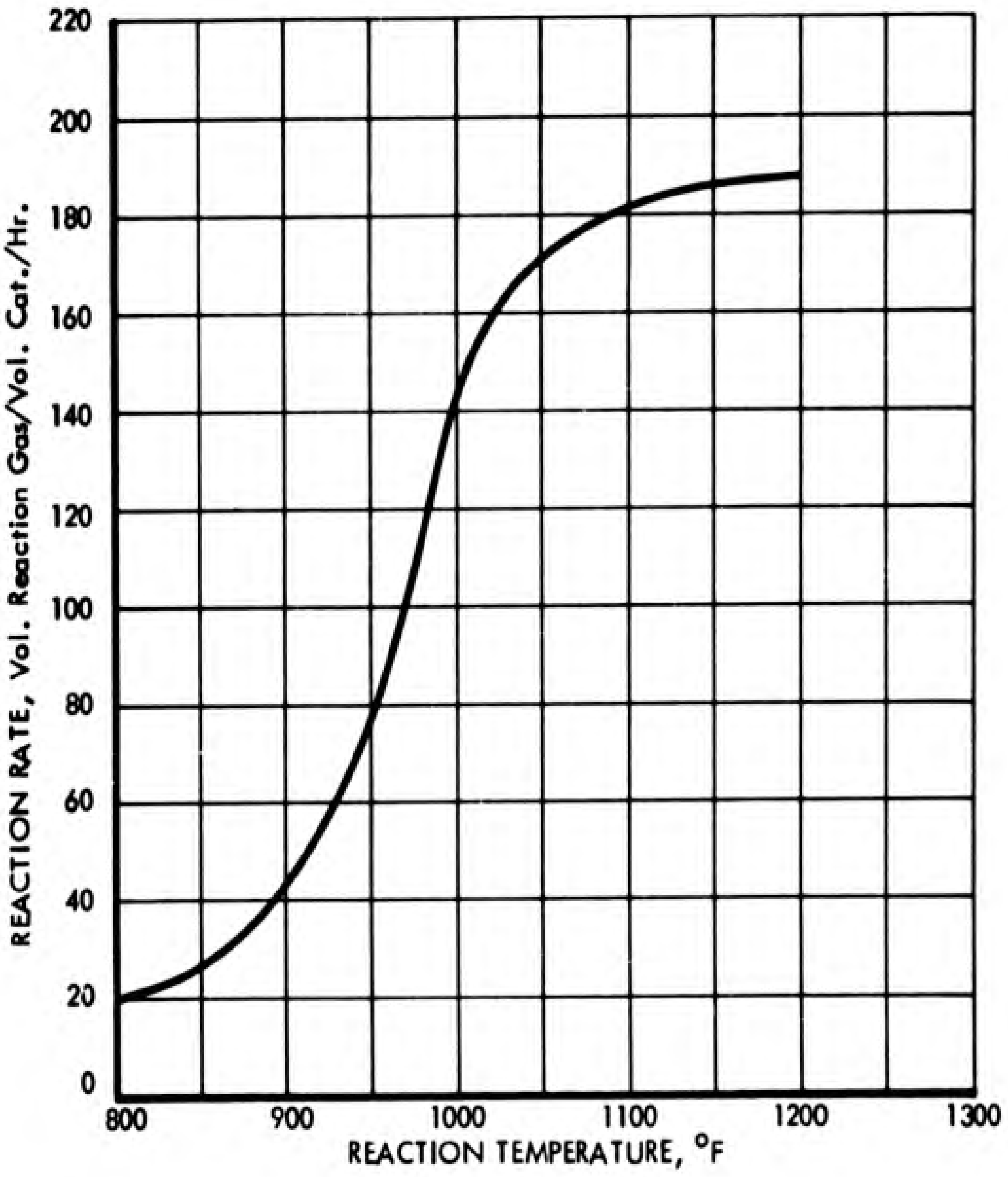


FIGURE 7-2

TABLE 7-4

EFFECT OF RECYCLE GAS COMPOSITION ON REACTION RATE - G-52 CATALYST

(Temperature = 800°F; Recycle Rate = 6.7 l./min.; Condenser Water Temperature = 71°F)

		Reaction Rate		Gas Analysis					
Date	Time	Ml/min.	Vol./vol. cat./hr.	H_2	N_2	CH_4	CO	CO_2	Atom Ratio H/O
10-25-62	0848	35	4.3	2.0	3.1	3.0	3.5	88.4 (diff.)	.09
	1163	100	11.5	2.5	2.9	12.7	4.5	77.4 (diff.)	.35
	1332	110	12.7	2.5	3.0	20.2	3.0	71.3 (diff.)	.59
	1532	150	17.3	3.0	3.3	22.5	3.5	64.5	.72
	1720	190	21.9	3.8	3.4	25.5	4.0	62.0	.86

TABLE 7-5

EFFECT OF RECYCLE GAS COMPOSITION ON REACTION RATE - G-52 CATALYST

(Temperature = 1000°F; Recycle Rate = 6.7 l./min; Condenser Water Temp. = 71°F)

		Reaction Rate		Gas Analysis					
Date	Time	ml/min.	vol./vol. cat./hr	H_2	N_2	CH_4	CO	CO_2	Atom Ratio H/O
10-26-62	1410	500	57.7	7.5	.8	4.5	16	73	.20
"	1448	220	25.4	4.5	.9	2.0	15.0	76	.10
"	1507	300	34.6	7.5	.9	4.5	12.5	72	.21
"	1623	900	104.0	9.0	1.2	7.0	15.0	61.0	.34
"	1717	1300	150.0	16.0	1.2	25	11	38	1.52
10-27-62	1005	100	11.5	28 (diff.)	2.0	69	1	0	304
"	1125	100	11.5	19.0	1.2	66	4.5	7.0	16.3
"	1145	1000	115.5	21.0	1.5	49	9.0	14.0	6.43
"	1206	1200	138.5	18.5	1.6	36	12.0	25.0	2.95
"	1225	1200	138.5	14.5	1.5	27.5	12.5	39.5	1.52
10-29-62	1035	600	69.2	9.7	1.5	8.1	15.5	64.5	.36
"	1128	600	69.2	11.2	1.9	9.7	15.2	65	.42
"	1333	860	99.4	11.0	2.3	18.0	13.0	56.5	.75
"	1418	1050	121.2	18.5	2.5	44.0	8.0	27.2	3.41
"	1548	1200	138.5	15.0	2.8	46.5	8.5	28.7	3.28

TABLE 7-6

EFFECT OF RECYCLE GAS COMPOSITION ON REACTION RATE - G-52 CATALYST

(Temperature = 1200°F; Recycle Rate = 8.1 l./min.; Condenser Water Temperature = 76°F)

		Reaction Rate		Gas Analysis					
Date	Time	Ml/min.	Vol./vol. cat./hr.	H_2	N_2	CH_4	CO	CO_2	Atom Ratio H/O
10-30-62	0918	1500	173.2	42.7 (diff.)	1.7	29	15	12	5.12
	0945	1500	173.2	28.5	1.7	14	24.5	30.5	1.32
	1005	1020	117.8	20.0	1.9	7.7	30.5	35.5	.70
	1023	750	86.7	17.0	1.9	4.5	34.0	37.2	.48
	1042	490	56.6	13.5	1.9	2.7	36.7	40.7	.32
	1112	340	39.3	12.0	2.0	1.5	37.5	45.7	.23
	1142	250	28.9	8.5	2.1	1.7	35.5	49.3	.18
	1302	180	20.8	6.0	2.5	1.0	31.5	58.0	.11
	1433	100	11.5	5.5	2.6	0.5	32.0	56.0	.09

The problem of graphically presenting the date in Tables 7-4, 7-5, and 7-6 presents some difficulty because of the multiple components in the gas composition. The approach that has been used is to calculate the atom ratio of hydrogen to oxygen in the recycle gas and plot this against reaction rate. This approach appears to be justified by the fact that the reaction that we seek to promote is that between hydrogen and oxygen to form water. Thus, assuming that there is some sort of approach to equilibrium in the reacting gases, the primary concern is how much oxygen and hydrogen are present. If we consider the carbon to be a carrier of oxygen and hydrogen, when it is in the gas phase, then the ratio of hydrogen to oxygen uniquely defines the gas composition as far as its water-forming potential is concerned. The hydrogen/oxygen atom ratios have been calculated for the gas compositions shown in Tables 7-4, 7-5 and 7-6 and are presented therein.

The reaction rate versus hydrogen/oxygen atom ratio (H/O) data from Tables 7-4, 7-5, and 7-6 are shown graphically in Figure 7-3. If we take the curves in Figure 7-3 at face value, they indicate that at 800°F, the maximum reaction rate is obtained at an H/O value somewhere above 0.8. At 1000°F, the maximum is at about 2, while at 1200°F, it is at about 2.6.

Under favorable equilibrium conditions, one would expect the maximum reaction rate at an H/O value of about 2. The high value for the maximum at 1200°F is evidently due to a mass action effect on reaction 7 of Figure 4-1, tending to drive it to completion in spite of the relatively unfavorable equilibrium at this high temperature. The fact that at low H/O values (below 1) the reaction rate at 1000°F appears to be higher than that at 1200°F is probably another aspect of this same effect. The indicated highest reaction of over 200 volumes/volume of catalyst per hour is supported by actual measured reaction rate data for which no corresponding analysis was obtained.

7.2.2.3 The Effect of Recycle Rate and Recycle Gas Water Content on the Reaction Rate of G-52 Catalyst

Data on the effect of recycle rate on the reaction rate of G-52 catalyst were obtained at 1000°F, with recycle gas that was dried in the usual manner by condensing the water at tap-water temperature (78°F), and with recycle gas dried by passing it over Dririte, which removes virtually all the water. The results

EFFECT OF RECYCLE GAS COMPOSITION ON REACTION RATE
(520 Ml. of G-52 Catalyst)

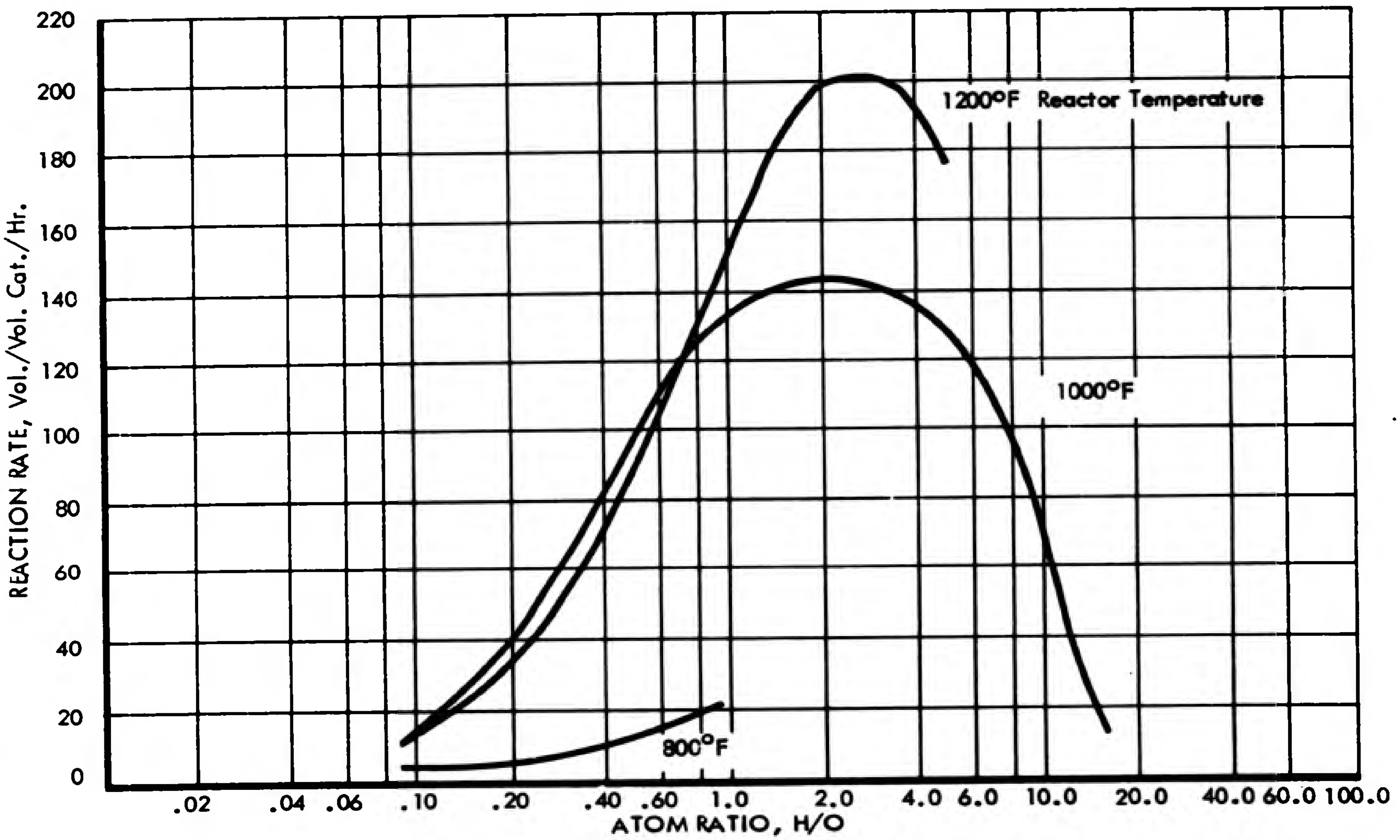


FIGURE 7-3

obtained are presented in Table 7-7 and shown graphically in Figure 7-4. It is evident that when using normal methods of removing the water (calculated 3.3% water remaining), the reaction rate can be about doubled by increasing the recycle rate from 5.5 to 9.5 liters/min. The actual increase is about the same when all the water is removed. In both cases the effect of increasing the recycle rate levels off at about 9 to 10 liters/min.

The effect of reducing the water content from 3.3% to zero is very marked at the high recycle rates, but less marked at the lower rates. The data show that by removing all the water and increasing the recycle rate, the reaction rate can be made almost triple that normally obtained at a recycle rate of about 5.5 liters/min.

7.2.3 Carbonyl Iron Catalyst

The parameters investigated with carbonyl iron catalyst were (1) the effect of recycle gas composition, (2) the effect of recycle rate, and (3) the effect of the water content of the recycle gas on the reaction rate.

7.2.3.1 The Effect of Recycle Gas Composition

Some data on the effect of recycle gas composition on reaction rate were obtained at 1100°F in runs 15, 18 and 19. In run 15 this was done by starting with a hydrogen rich mixture and feeding a carbon dioxide rich feed gas. In run 18, it was done by starting with a carbon dioxide rich mixture and feeding a hydrogen rich feed gas. In both cases analyses were taken at regular intervals and the corresponding reaction rates noted. The results obtained with run 15 are presented in Table 7-8 and shown graphically in Figure 7-5. The results obtained with run 18 are presented in Table 7-9 and shown graphically in Figure 7-6.

In Figures 7-5 and 7-6, the actual gas compositions are plotted against elapsed time. To show the effect of H/O atom ratio on reaction rate data from runs 15 and 19 are presented in Table 7-10 and shown graphically in Figure 7-7.

When Figure 7-7 is compared with Figure 7-3, it is evident that the carbonyl iron catalyst is equivalent to the G-52 catalyst in activity for corresponding temperatures. However , it is interesting to note that the H/O atom ratio where the maximum reaction rate is obtained is about 3 for the G-52 catalyst at 1200°F, as

TABLE 7-7

EFFECT OF RECYCLE RATE AND WATER CONTENT OF RECYCLE GAS ON REACTION RATE

[Temperature = 1000°F; 520 ml. of G-52 Catalyst; Temperature of Condenser Water = 78°F; Recycle Gas Composition held approximately constant(a)]

Volume % Water (Calculated)	Recycle Rate, Liters/Min.	Reaction Rate Liters/min.	Reaction Rate Vol./vol.Cat./Hr.
3.3	9.7	1.3	150.2
3.3	8.1	1.25	144.5
3.3	6.7	1.09	125.9
3.3	5.4	.67	77.4
0.0	10.1	1.75	202
0.0	9.4	1.77	204.5
0.0	8.1	1.66	191.8
0.0	6.7	1.20	138.7

(a) Composition of Recycle Gas at:

		Beginning of Experiment	End of Experiment
Volume %	H_2	18.5	15.0
	N_2	2.47	2.85
	CH_4	44.0	46.5
	CO	8.0	8.5
	CO_2	27.2	28.7

EFFECT OF RECYCLE RATE AND WATER CONTENT OF RECYCLE GAS ON REACTION RATE

(Reaction Temperature = 1000°F; 520 Ml. of G-52 Catalyst)

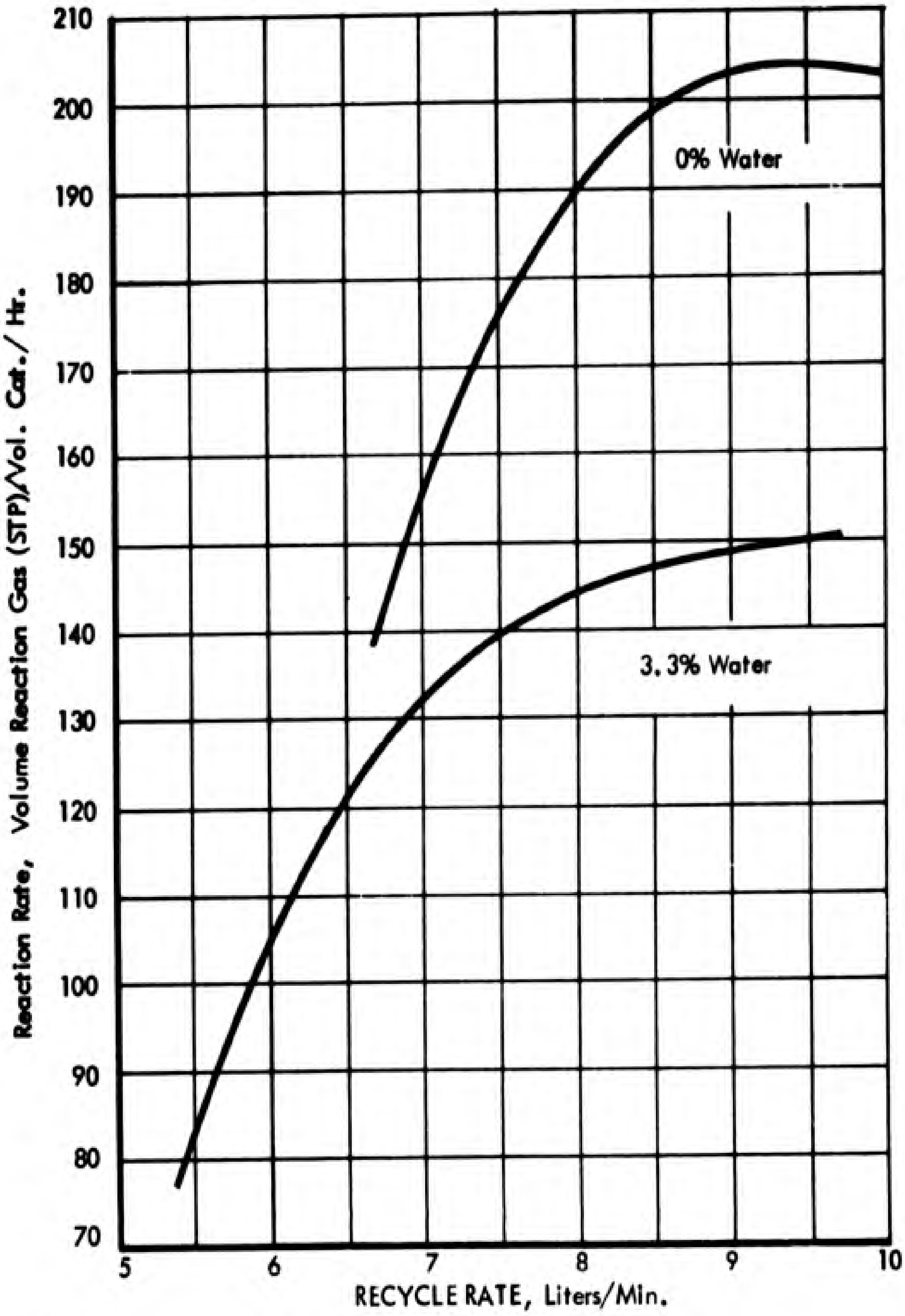


FIGURE 7-4

TABLE 7-8

RUN NO. 15 - EFFECT OF RECYCLE GAS COMPOSITION ON REACTION RATE OF CARBONYL IRON CATALYST AT 1100°F

Time		Reaction Rate		Recycle Gas Composition - Vol %									
				H_2		N_2		CH_4		CO		CO_2	
Real	Elapsed (min)	ml/min	vol/vol cat/ Hr (a)	obs	corr(b)	obs	corr(b)	obs	corr(b)	obs	corr(b)	obs	corr(b)
1426	0	970	112	58.8	62.6	6.2	—	24.0	25.6	5.5	5.9	5.5	5.9
1535	69	1550	179	46.9	50.1	6.4	—	20.0	21.4	12.7	13.6	14.0	14.9
1558	92	1100	127	40.7	43.5	6.4	—	14.0	15.0	17.5	18.7	21.4	22.8
1617	111	540	62	29.0	31.0	5.4	—	11.0	11.7	23.5	25.1	30.2	32.2
1636	130	522	60	27.0	29.8	5.0	—	9.0	9.9	23.5	25.9	31.2	34.4

(a) Volume of reaction gas (33.3% CO_2 and 66.7% H_2 at room temperature) per volume of catalyst per hour. The volume of catalyst in this run was 520 ml.

(b) Composition excluding nitrogen.

EFFECT OF RECYCLE GAS COMPOSITION ON REACTION RATE
RUN # 15 - CARBONYL IRON CATALYST
(TEMP. = 1100°F, RECYCLE RATE = 7.7 LITERS/MIN., COOLING WATER AT 74°F)

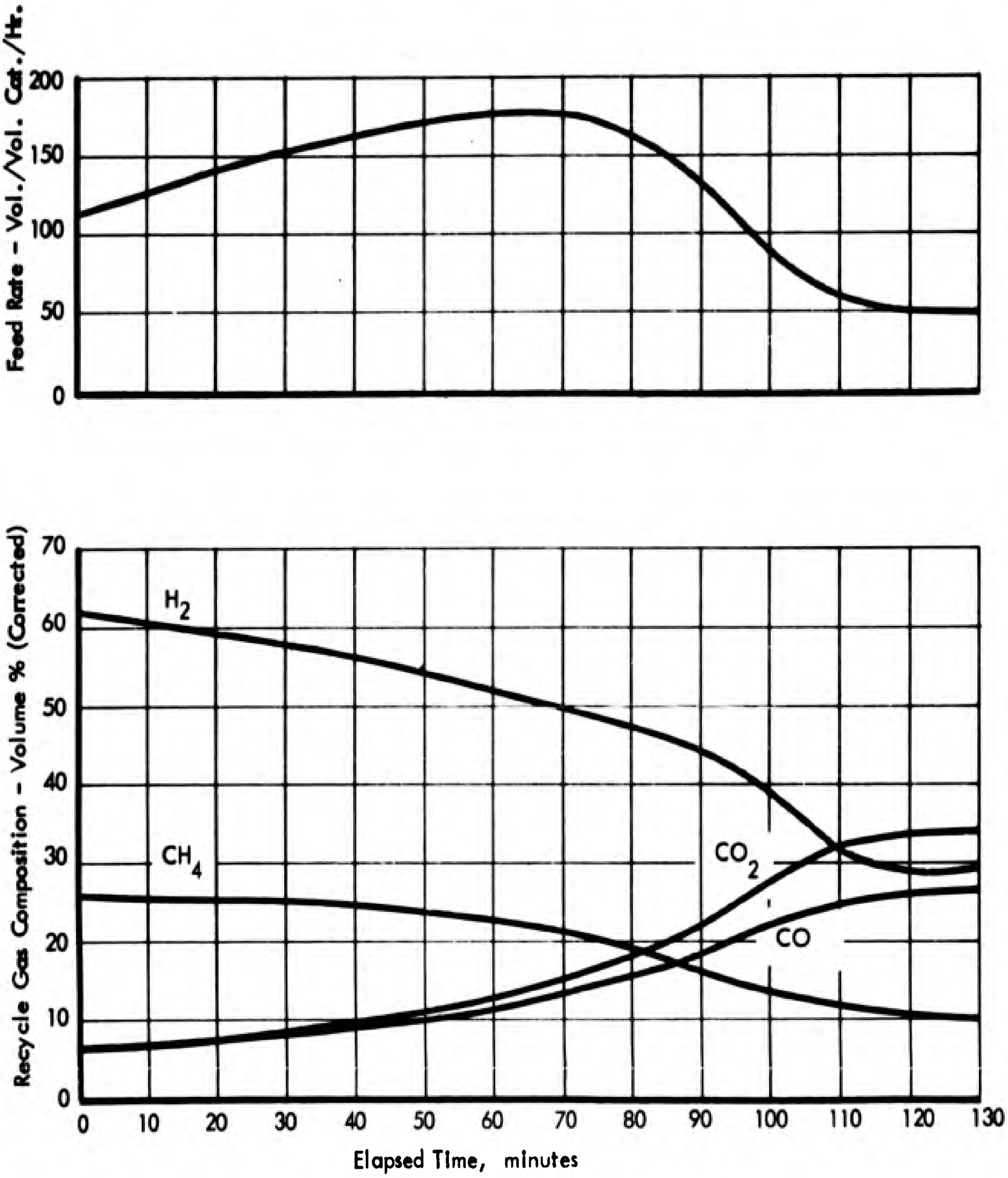


FIGURE 7-5

TABLE 7-9

RUN NO. 18 - EFFECT OF RECYCLE GAS COMPOSITION ON REACTION RATE OF CARBONYL IRON CATALYST AT 1100°F

Time		Reaction Rate		Recycle Gas Composition - Vol %									
			vol/vol cat/	H_2		N_2		CH_4		CO		CO_2	
Real	Elapsed (min)	ml/min	Hr[a]	obs	corr[b]	obs	corr[b]	obs	corr[b]	obs	corr[b]	obs	corr[b]
0904	0	800	92	22.4	23.6	6.1	—	14.0	14.7	26.0	27.3	32.8	34.4
1003	59	940	108	25.2	26.2	6.2	—	11.5	11.9	26.7	27.7	33.0	34.2
1033	89	1020	118	28.5	29.1	6.3	—	12.2	12.4	27.5	28.1	29.8	30.4
1103	119	1080	125	27.3	29.0	5.8	—	12.9	13.7	26.7	28.3	27.3	29.0
1133	149	1100	127	25.6	27.2	5.9	—	13.0	13.8	27.2	28.9	28.3	30.1
1234	210	1130	130	30.1	31.9	5.7	—	15.7	16.6	24.0	25.4	24.5	26.0
1303	239	1150	133	29.4	31.1	5.4	—	18.2	19.2	23.0	24.3	24.0	25.4
1333	269	1160	134	30.5	32.2	5.2	—	19.5	20.6	22.5	23.7	22.3	23.5
1403	299	1160	134	30.1	31.8	5.2	—	20.5	21.7	22.5	23.7	21.7	22.8
1433	329	1180	136	33.3	35.0	4.7	—	20.8	21.8	21.5	22.5	19.7	20.7
1504	360	1190	137	34.0	35.7	4.8	—	22.0	23.1	21.5	22.6	17.7	18.6
1604	420	1270	149	36.1	37.8	4.4	—	24.0	25.1	19.5	20.4	16.0	16.7
1710	486	1360	157	36.7	38.1	3.6	—	27.0	28.0	18.2	18.9	14.5	15.0
2203	779	1070	123	36.9	37.5	1.6	—	34.0	34.6	14.8	15.0	12.7	12.9

(a) Volume of reaction gas (33.3% CO_2 and 66.7% H_2 at room temperature) per volume of catalyst per hour. The volume of catalyst in this run was 520 ml.

(b) Composition excluding nitrogen.

EFFECT ON RECYCLE GAS COMPOSITION ON REACTION RATE
RUN # 18 - CARBONYL IRON CATALYST
(TEMP. = 1100°F, RECYCLE RATE = 7.7 LITERS/MIN., COOLING WATER TEMP. = 61°F)

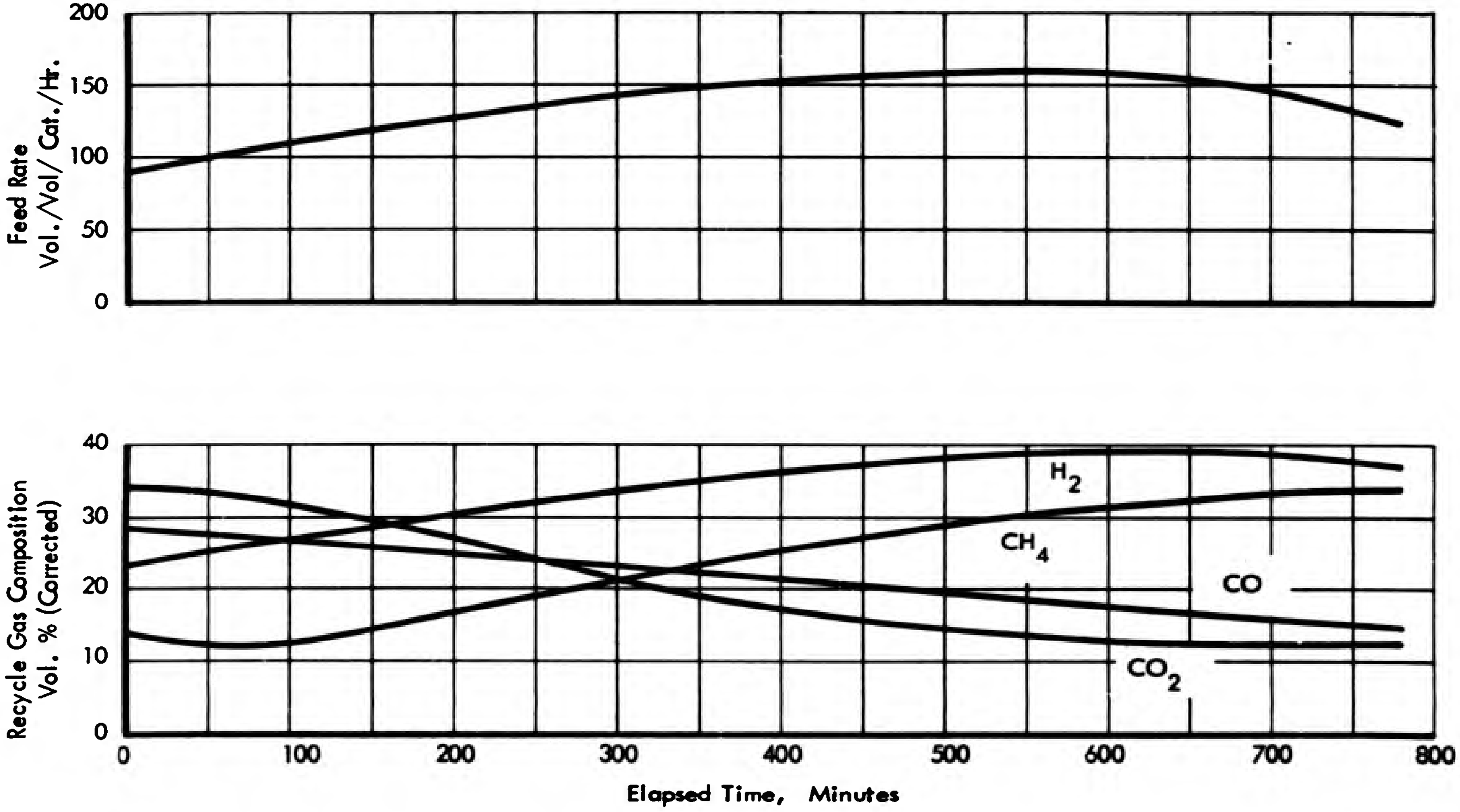


FIGURE 7-6

TABLE 7-10

EFFECT OF RECYCLE GAS COMPOSITION ON REACTION RATE

(CARBONYL IRON CATALYST: REACTION TEMPERATURE = 1100° F; RECYCLE RATE = 7.8 LITERS/MIN; CONDENSER WATER TEMPERATURE = 65° F)

				Reaction Rate		Gas Analysis					
Run No.	Volume of Catalyst–ml.	Date	Time	ml/min	Vol/Vol Cat/Hr	H_2	N_2	CH_4	CO	CO_2	ATOM Ratio (H/O)
15	520	11-8-62	1426	970	112	58.8	6.2	24.0	5.5	5.5	13.0
"	"	"	1535	1550	179	46.9	6.4	20.0	12.7	14.0	4.3
"	"		1558	1100	127	40.7	6.4	14.0	17.5	21.4	2.3
"	"		1617	540	62	29.9	5.4	11.0	23.5	30.2	1.2
"	"		1636	600	69	27.0	5.0	9.0	23.5	31.2	0.96
19	260	12-4-62	1600	900	208	32.0	2.5	23.0	23.0	19.5	2.6
"	"	12-5-62	1118	300	67	63.3	6.0	28.2	2.1	0.4	32.5
"	"	"	1319	1530	353	50.8	6.3	21.5	12.7	8.7	6.2
"	"	"	1423	950	219	35.9	6.6	14.5	23.5	19.5	2.1
"	"	"	1603	1050	242	37.8	7.2	14.5	22.2	18.3	2.3

EFFECT OF RECYCLE GAS COMPOSITION ON REACTION RATE CARBONYL IRON CATALYST AT 1100°F

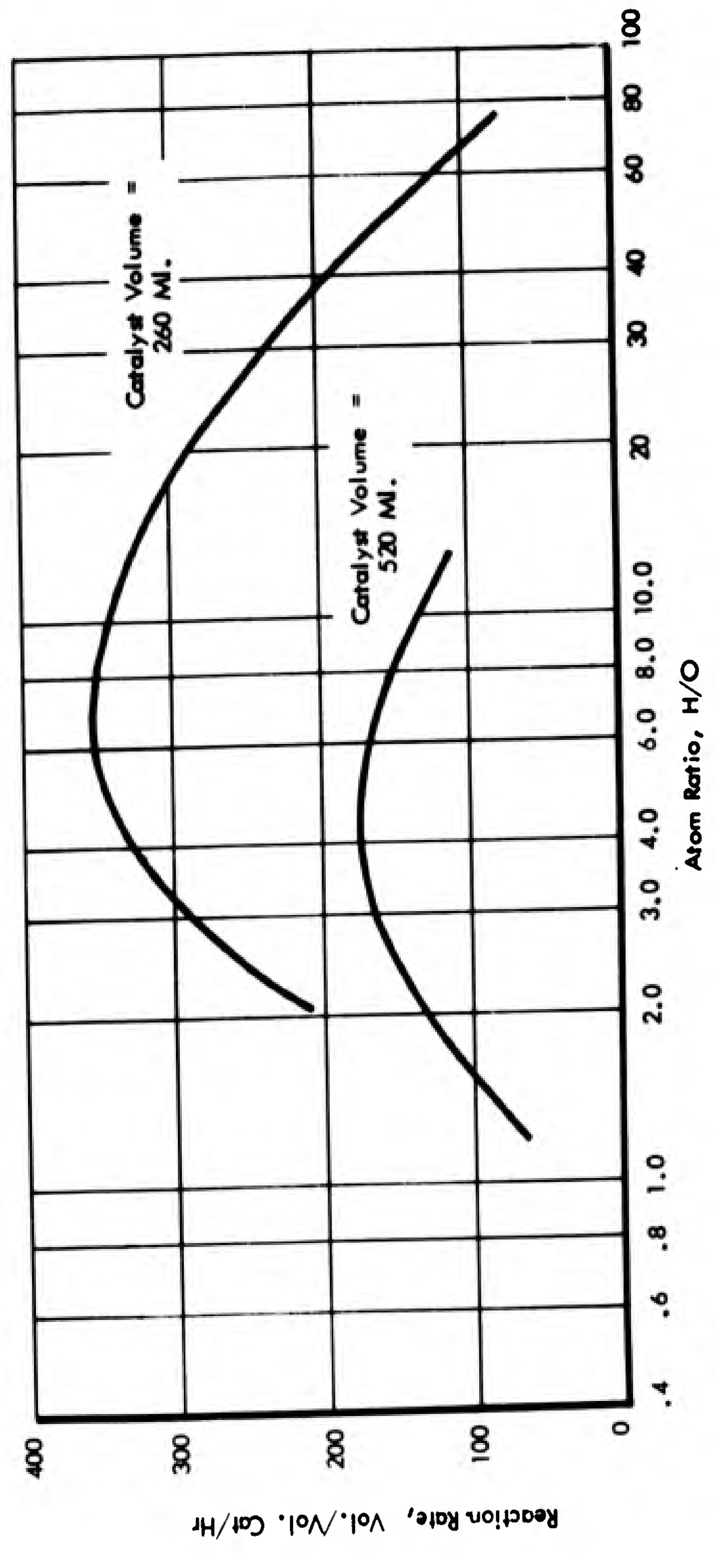


FIGURE 7-7

compared to 4 to 6 for the carbonyl iron catalyst at 1100°F. The difference is believed due to differences in the nature of the catalysts.

The fact that the G-52 catalyst and the carbonyl iron catalyst show equivalent activity is believed due to the fact that both catalysts bring the reaction gases essentially to equilibrium on each pass. Actually there are indications that the carbonyl iron catalyst is the more active, as will be brought out in Section 7.2.3.2.

7.2.3.2 The Effect of Recycle Rate and Water Content of the Recycle Gas on the Reaction Rate of Carbonyl Iron Catalyst

During run 15 data were obtained on the effect of recycle rate on reaction rate, both with normal water contents of the recycle gas, and with the recycle gas completely dried by passing through a container of Dririte. The results are presented in Table 7-11 and shown graphically in Figure 7-8. During the time these data were being collected, an effort was made to keep the composition of the recycle gas constant at the composition shown in Table 7-11.

It is interesting to note that the recycle rate versus reaction rate curves obtained with carbonyl iron catalyst during run 15 and shown in Figure 7-8 are essentially straight lines, whereas those obtained with G-52 catalyst and shown in Figure 7-4, tend to level off at the higher recycle rates. While the reaction rate level is higher in the case of the G-52 catalyst, this is attributed to the fact that the G-52 catalyst was operating on a recycle gas composition that was more optimum for it. The fact that the reaction rate of the G-52 catalyst tends to level off at the higher recycle rates indicates that the catalyst is no longer able to bring the gases approximately to equilibrium on each pass because of the short contact time. The fact that the carbonyl iron catalyst does not show this effect is an indication that it is the more active. As a matter of fact, the results obtained with run 19 indicate that the same result would have been obtained with only half as much carbonyl iron catalyst, and as far as is known now, even less might be sufficient.

TABLE 7-11

EFFECT OF RECYCLE RATE AND WATER CONTENT OF THE RECYCLE GAS ON REACTION RATE OF CARBONYL IRON CATALYST

(Temperature = 1000° F, Cooling Water Temperature = 74° F)

Water Content	Recycle Rate		Feed Rate	
Vol %	Rotometer Reading	Liters Min	ml/min	vol/vol cat/hr
2.82	40	5.4	120	13.9
2.82	50	6.7	210	24
2.82	60	8.1	255	29.4
2.82	70	9.4	340	39
0	40	5.4	360	42
0	50	6.7	550	63
0	60	8.1	670	77
0	70	9.4	800	92

Note: Recycle Gas Composition, Vol % H_2 = 22.0
N_2 = 4.0
CH_4 = 26.0
CO = 16.2
CO_2 = 26.8

EFFECT OF RECYCLE RATE AND WATER CONTENT OF THE RECYCLE GAS ON REACTION RATE

RUN # 15 - CARBONYL IRON CATALYST
(REACTOR TEMP. = 1000°F, COOLING WATER TEMP. = 74°F)

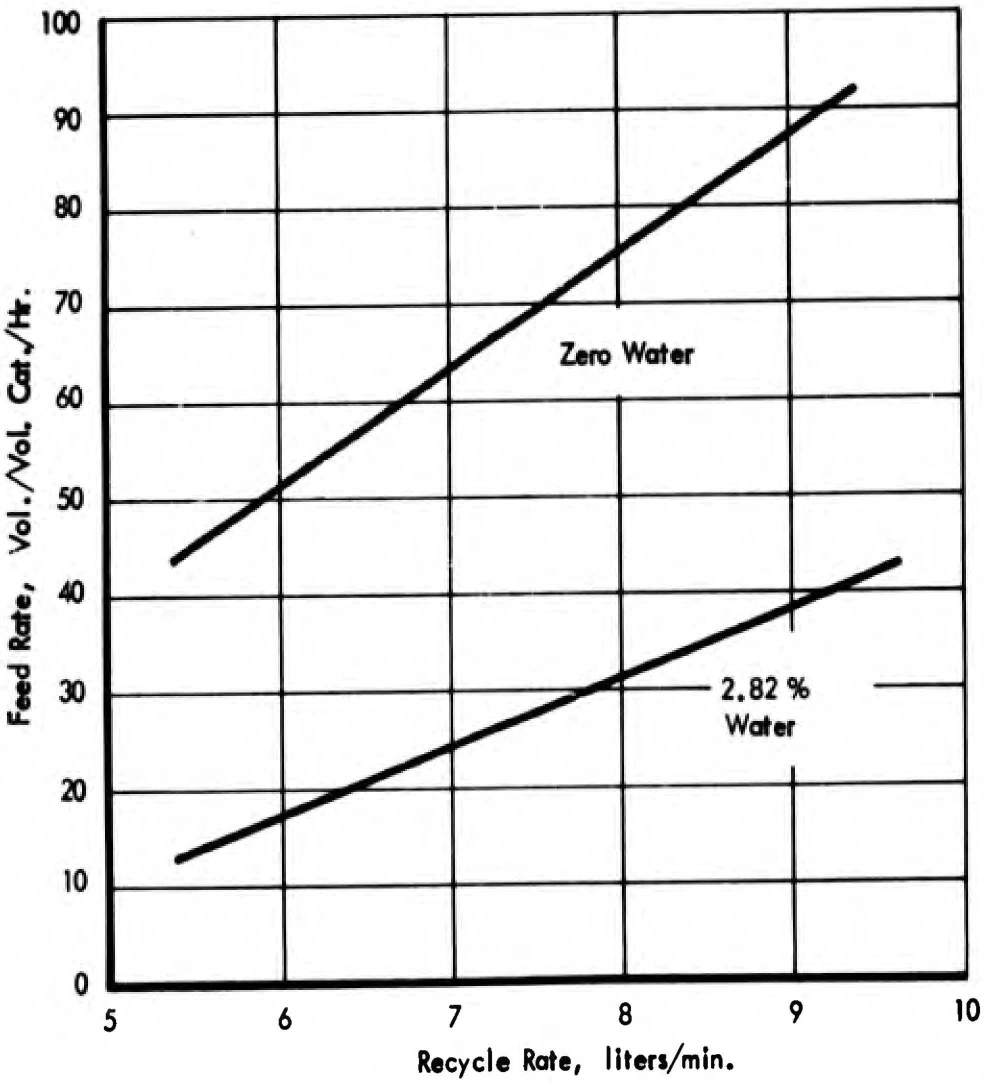


FIGURE 7-8

8.0 SYSTEM FOR ATMOSPHERIC CONTROL OF A 100 MAN SUBMARINE

Contract Nonr 3431(00)(FBM) calls for a preliminary design of a 100 man capacity unit stressing compactness, ease of maintenance and reliability. This design was to be based on the results of experiments conducted on the one man fluidized catalyst bed equipment. In pursuing this design study, the requirements have been first defined. Next, the special problems of excess hydrogen and carbon and water use or disposal have been considered. Finally, the preliminary design of a 100 man capacity unit is presented.

8.1 Requirements

The amount of oxygen consumed and carbon dioxide produced by the respiration of a crew member depends on many factors, the most important of which are his degree of activity and his respiratory quotient (RQ). The latter depends on the type of food consumed and is the molar (volume) ratio of carbon dioxide produced to oxygen consumed. Since one mole of oxygen will react with one mole of solid carbon to produce one mole of carbon dioxide, it follows that the moles (volume) of oxygen equal the moles (volume) of carbon dioxide if this is the only reaction involved. Actually the RQ is always less than one, which means that the volume of carbon dioxide produced is less than that of the oxygen consumed. This reflects the fact that the food oxidized in the body contains both carbon and hydrogen and the oxidation of these materials accounts for virtually all the oxygen consumed by respiration. Since that part of the oxygen used to oxidize hydrogen to water does not produce carbon dioxide, it follows that the volume of carbon dioxide produced will be less than that of the oxygen consumed.

The normal consumption of oxygen by a submarine crewman over an extended period is given as 1 scf per hour while the normal RQ is given as 0.85 (Reference 2). Based on these data, the amounts of carbon dioxide, hydrogen, and oxygen involved in a system that reduces the carbon dioxide with hydrogen and produces oxygen by electrolysis is given in Table 8-1 for a 100 man crew. It is evident that there will be some 720 scf of hydrogen in excess produced every day. In other words, only 85% of the hydrogen produced by the electrolysis of water is consumed by the reduction of CO_2. The problem of how to handle this imbalance is discussed in the following sections.

TABLE 8-1

CARBON DIOXIDE, OXYGEN, AND HYDROGEN INVOLVED IN THE OPERATION OF A 100 MAN ENVIRONMENTAL CONTROL SYSTEM

Gas	CO_2	O_2	H_2
St Cu Ft/Hr	85	100(a)	200(a)
St Cu Ft/Day	2040	2400	4800
Lb/Day	250	214	26.75
Reduction of CO_2 St Cu Ft/Day	2040		4080
Excess Hydrogen St Cu Ft/Day			720

(a) Assuming that oxygen and hydrogen are produced by the electrolysis of water.

8.2 The Excess Hydrogen Problem

The most obvious disposition of the excess hydrogen is to vent it overboard as is now being done with both hydrogen and carbon dioxide. It can be argued that with this mode of operation no carbon dioxide and only 15% of the hydrogen would be vented, hence the detection hazard should be materially reduced. However, for purposes of the present discussion, it will be assumed that it is permissible to vent nothing but water overboard. Hence this solution is unacceptable.

Another obvious solution is to store the hydrogen on board in pressure vessels, but this is not attractive because of the large volumes and weights of the pressure vessels involved. However, hydrogen can be fixed by reaction with carbon to form hydrocarbons or oxygenated hydrocarbons that can be stored more readily. It can also be reacted with nitrogen to form ammonia that is readily storable. Another possible solution is to not produce the excess hydrogen in the first place. This can be done by carrying on board 15% of the oxygen required for respiration. The production of the remaining 85% of the required oxygen by the electrolysis of water will result in the production of just sufficient hydrogen to reduce the carbon dioxide produced. These three possibilities have been considered in a preliminary way and are discussed in some detail in the following sections.

8.2.1 The Production of Hydrocarbons

While it is feasible to produce either hydrocarbons, or oxygenated hydrocarbons, only the former have been considered for present purposes because of the generally greater weight and volume of the oxygenated hydrocarbons per unit of hydrogen carried. There are well known processes for producing hydrocarbons from synthesis gas, which is a mixture of carbon monoxide and hydrogen. Since such mixtures are formed rather readily from carbon dioxide and hydrogen by the water gas shift reaction, it is evident that hydrocarbons can be readily formed starting with a mixture of the latter gases. In fact, the formation of methane always occurs to a greater or less extent in the process of reducing carbon dioxide to carbon and water. However, methane is difficult to separate from the other reaction gases and unsuitable for storage. It would therefore be desirable to form higher molecular weight hydrocarbons. In the Fischer Tropsch type synthesis higher molecular weight hydrocarbons can be formed, although the temperatures (200 to 300°C, 392 to 572°F) are considerably lower than those found advantageous for the reduction of carbon dioxide with hydrogen. However, at least in principle, it can be said that the excess hydrogen can be combined with carbon to form high molecular weight (low vapor pressure) liquid hydrocarbons that can readily be stored on board. If such hydrocarbons have a formula that can be represented by $(CH_2)_x$ and a specific gravity of 0.8 at the temperature of storage, (assumed to be 100°F), then the material produced on a 60 day mission, using the excess hydrogen, would occupy a volume of 33.9 cu ft and would weigh 1690 lbs. The additional carbon produced would weigh 2643 lb and would occupy a volume of 48.1 cu ft, assuming a bulk specific gravity of 0.9. The total volume occupied by stored material for the system is then 33.9 + 47.1 = 81.0 cu ft. No attempt has been made to estimate the volume of excess equipment that would be required to make and isolate the hydrocarbon, but it is expected that it would be considerable. Weight and volume data on the hydrocarbon system are summarized in Table 8-2, along with similar data on the other systemsconsidered.

8.2.2 The Production of Ammonia

The excess hydrogen can be combined with nitrogen from the submarine atmosphere to produce ammonia that can readily be stored on board. The nitrogen consumed during a 60 day cruise would amount to 40.3 moles (14,500 scf). If the partial pressure of oxygen was held constant and the atmospheric pressure in the submarine allowed to decrease as the nitrogen is consumed and if then we assume a submarine atmosphere volume of 700 cu ft/man (Reference 2) the pressure would drop from 14.7 to 11.6 psi during a 60 day cruise.

An estimate of the equipment required to produce the necessary ammonia indicates that it would occupy a volume of 6 cu ft and weign about 400 lbs. Data on the weight and volume of ammonia produced are included in Table 8-2.

8.2.3 Oxygen Storage

If only enough hydrogen is produced by electrolysis to reduce the carbon dioxide produced by the crew, then the oxygen produced by electrolysis will be 85% of that required, and the other 15% must be stored on board. This amounts to 2250 lbs for a 60 day cruise. While this can be stored as a gas under pressure, its storage as liquid oxygen (LOX) minimizes the weight and volume. Data on weights and volumes of LOX required for this system are included in Table 8-2.

TABLE 8-2

MATERIAL STORAGE FOR VARIOUS SOLUTIONS OF THE EXCESS HYDROGEN PROBLEM

(Based on a 100 man crew on a 60 day cruise)

Solution	Hydrogen Stored as Hydrocarbon	Hydrogen Stored as Ammonia	Excess Hydrogen Not Produced
Liquid Stored	Hydrocarbon	Ammonia	LOX
Density (lb/cu ft)	50 (100°F)	36.4(100°F)	71
Wt for 60-day cruise(lb)	1690	1363	1926
Liquid Volume (cu ft)	33.8	37.4	27.1
Amount of Additional Equipment Needed	Large	Large	Negligible
Carbon Produced on a 60-day cruise (lb)	2643	4090	4090
Volume at 56 lb/cu ft	47.1	73	73
Total Storage Volume Assuming that carbon is stored on board	80.9	110.4	100.1
Total Storage Volume Assuming that Carbon is ejected overboard	33.8	37.4	27.1
Power for electrolysis (KW)(a)	17.5	17.5	14.9

(a) Assuming 100% efficiency for the electrolytic cell.

One advantage of using the stored oxygen system that is not readily apparent is the lower power consumption due to the fact that the amount of water decomposed to oxygen and hydrogen by electrolysis is decreased by 15%.

Looking at the problem broadly, it appears that the stored oxygen system is the best solution to the excess hydrogen problem. It compares favorably with the other systems on a volume basis if carbon is not stored on board, or if the carbon storage space is discounted because of the employment of the space originally used for food. The oxygen storage has the advantage of simplicity and high reliability. The extra oxygen can be looked upon as a supplement to the regular emergency oxygen supply and gives the submarine commander more flexibility and a larger factor of safety in managing his oxygen resources.

8.3 The Use and Disposal of Carbon

If all the carbon dioxide produced by a 100 man crew on a 60 day cruise is reduced to carbon the weight of carbon produced will be 4090 lbs. The carbon would be expected to have a crystal specific gravity of about 1.8. If tightly packed it would be expected to have a bulk specific gravity of 0.9, which would correspond to a volume of 73 cu ft. The disposition of this carbon affects the design of the equipment, since, if the carbon is to be stored on board, then storage space must be provided, but this need not be opened during the cruise. On the other hand, if the carbon is thrown overboard or employed on board for odor control, or for otherpurposes, then provision must be made for removing carbon from the equipment during the cruise.

The posiibility of using at least part of the carbon for the control of odors and aerosols in the submarine atmosphere is particularly intriguing. It is indicated (Reference 2) that the amount of carbon required for odor control is one pound of carbon for each 75 cu ft of ship's floodable volume. If this volume is taken to be 700 cu ft/man, then some 940 lbs of carbon would be required. Since about four times this much carbon is produced during a 60 day cruise, it is evident that all of the carbon necessary for odor control can be generated on board, assuming that this carbon is effective for odor removal. While the carbon produced by the reduction of carbon dioxide has not been tested for effectiveness in odor control as far as is known, there is every indication that it would be highly effective. It is extremely finely divided and should be highly activated as formed.

Since all of the carbon will presumably not be needed for odor control, it is possible that by using larger, more densely packed filters, carbon could also be used for aerosol control, thus doing away with the electrostatic filters now being employed (Reference 2).

If it is not feasible to use the carbon on board, then there is a possibility that it can be thrown overboard without involving a detection risk. Since carbon is about twice as heavy as water, it should sink rapidly. Since it is completely insoluble in water, it should leave no detectable trace in the water. It has been suggested that the carbon could be fed into the garbage ejector from which it would be discharged overboard. The carbon could also be discharged into the sanitary tanks, or the bilge, where it would occupy only about half the volume it would occupy in dry storage, since in the former cases the space between the carbon particles would be occupied by liquid.

8.4 The Use and Disposal of Water

The water that has been produced in the experimental equipment has no odor or taste and appears to be a good grade of distilled water. It is assumed to be potable and hence will contribute to the ship's fresh water supply. It has been reported that about 15 gallons of fresh water per man day is required by a submarine crew. The amount of water produced by carbon dioxide reduction is 2.04 lb/man day. Thus while the amount of fresh water produced is only a small fraction of that needed, it might have special value as emergency drinking water in case the regular fresh water supply was accidently contaminated or was otherwise unavailable for drinking.

In case it is considered undesirable to use the water produced by the reduction of carbon dioxide, it need not be stored on board, since it can be discharged overboard without involving a detection hazard.

8.5 Preliminary Design of a 100 Man Carbon Dioxide Reduction Plant

A preliminary design has been made of a plant to reduce the carbon dioxide produced by a 100 man crew. The design requirements of compactness, ease of maintenance and reliability have been kept in mind in this design study. However, no effort has been made to optimize the design with respect to these characteristics. In the following presentation of the design, the flow plan is first considered, then the components and controls are described. Finally, volume, weight and material consumption estimates are presented.

8.5.1 Schematic of Flow Plan

A proposed flow plan is presented in Figure 8-1. This figure also presents flow rates, temperatures, reaction gas composition and electric power consumption data at various points in the system. This flow plan is essentially the same as that used on the one-man experimental apparatus shown in Figure 5-1, except that the heat exchanger is placed before the filter in the reaction gas stream leaving the reactor. This change has been made for reasons that are set forth in the discussion of the heat exchanger in Section 8.5.3. A three dimensional layout drawing of the equipment is shown in Figure 8-1A.

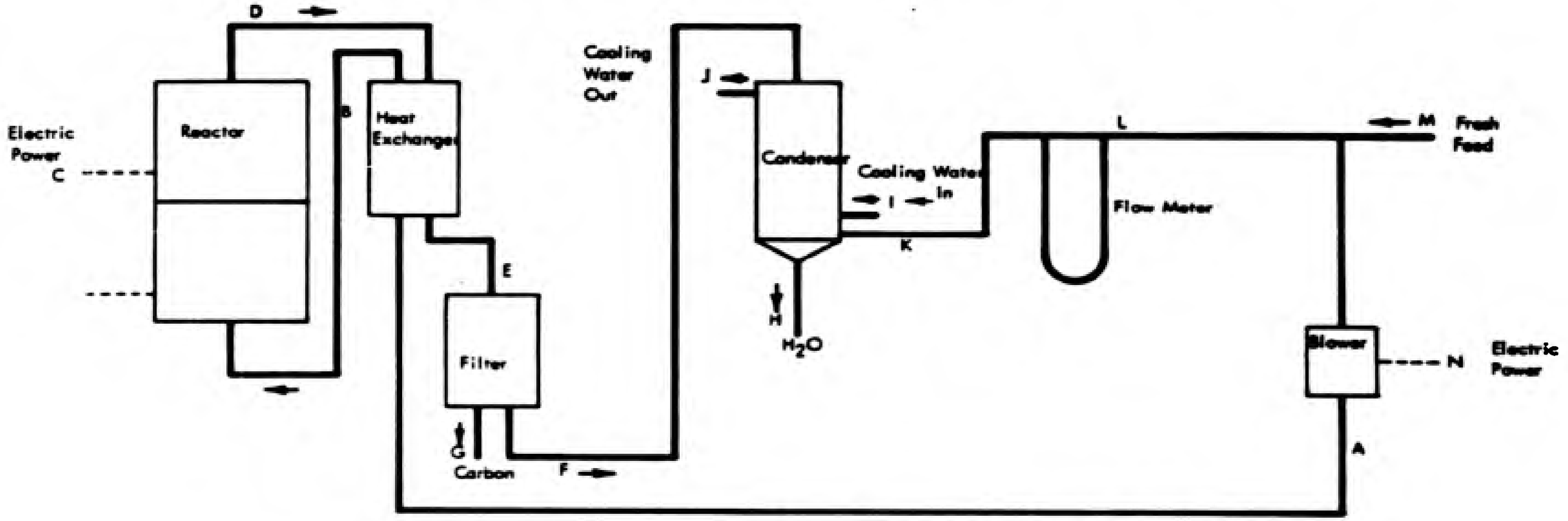
8.5.2 The Reduction Reactor

A conceptual design of a reactor to reduce the carbon dioxide produced by a 100 man crew is shown in Figure 8-2. The reactor has two fluid catalyst beds each 24 inches in diameter. This is a conservative design and would correspond to a 128 man unit, based on a scale-up of the 3 inch diameter one man unit.

The amount of catalyst used in this reactor can vary from a depth of 2 to 6 inches, depending on catalyst activity. With the carbonyl iron catalyst a depth of 3 inches appears to be reasonable. This corresponds to a catalyst volume of 1.57 cu ft and a weight of 226 lbs. A 3 inch grid entends from near the bottom of each compartment to near the top. The purpose of this grid is to keep the catalyst from flowing to one side of the reactor when the submarine rolls or pitches. Space is provided at the bottom of the grid so that catalyst can transfer from one grid space to another, but this transfer rate is relatively slow, so that the catalyst bed will not be unduly disturbed by say a 2 minute diving maneuver when the pitch may be so high as 30°.

The reaction gases are distributed over the bottom of each compartment of the reactor by a series of tubes spaced one inch apart and having orifices, one inch apart, along the length of the tubes. The reaction gases pass through these

FLOW PLAN AND TEMPERATURE, PRESSURE AND FLOW RATE DATA 100 MAN CO_2 REDUCTION PLANT



STATION	TEMP°F.	PRESSURE IN. of WATER	FLOW RATE - LB. MOLES/HR.						GAS COMPOSITION - VOL.%					ELECTRIC POWER (KW)	FLOW RATE LB./HR.
			H_2	CH_4	CO	CO_2	H_2O	C	H_2	CH_4	CO	CO_2	H_2O		
A	136	32	3.157	1.144	.729	1.040	.269	—	49.8	18.1	11.5	16.4	4.2	—	—
B	908	29	3.157	1.144	.729	1.040	.269	—	49.8	18.1	11.5	16.4	4.2	—	—
C	—	—	—	—	—	—	—	—	—	—	—	—	—	1.53	—
D	1100	13	2.670	1.144	.729	.796	.756	.243	43.8	18.8	11.9	13.1	12.4	—	—
E	328	10	2.670	1.144	.729	.796	.756	.243	43.8	18.8	11.9	13.1	12.4	—	—
F	328	3.5	2.670	1.144	.729	.796	.756	—	43.8	18.8	11.9	13.1	12.4	—	—
G	—	—	—	—	—	—	—	.243	—	—	—	—	—	—	2.92
H	—	—	—	—	—	—	.487	—	—	—	—	—	—	—	8.76
I	80	—	—	—	—	—	—	—	—	—	—	—	—	—	1650
J	90	—	—	—	—	—	—	—	—	—	—	—	—	—	1650
K	90	0.5	2.670	1.144	.729	.795	.269	—	47.6	20.4	13.0	14.2	4.8	—	—
L	90	0.0	2.670	1.144	.729	.796	.269	—	47.6	20.4	13.0	14.2	4.8	—	—
M	90	0.0	.487	—	—	.244	—	—	66.7	—	—	33.3	—	—	—
N	—	—	—	—	—	—	—	—	—	—	—	—	—	0.6	—

FIGURE 8-1

THREE DIMENSIONAL LAYOUT OF EQUIPMENT FOR THE REDUCTION OF CARBON DIOXIDE FOR A 100 MAN CREW

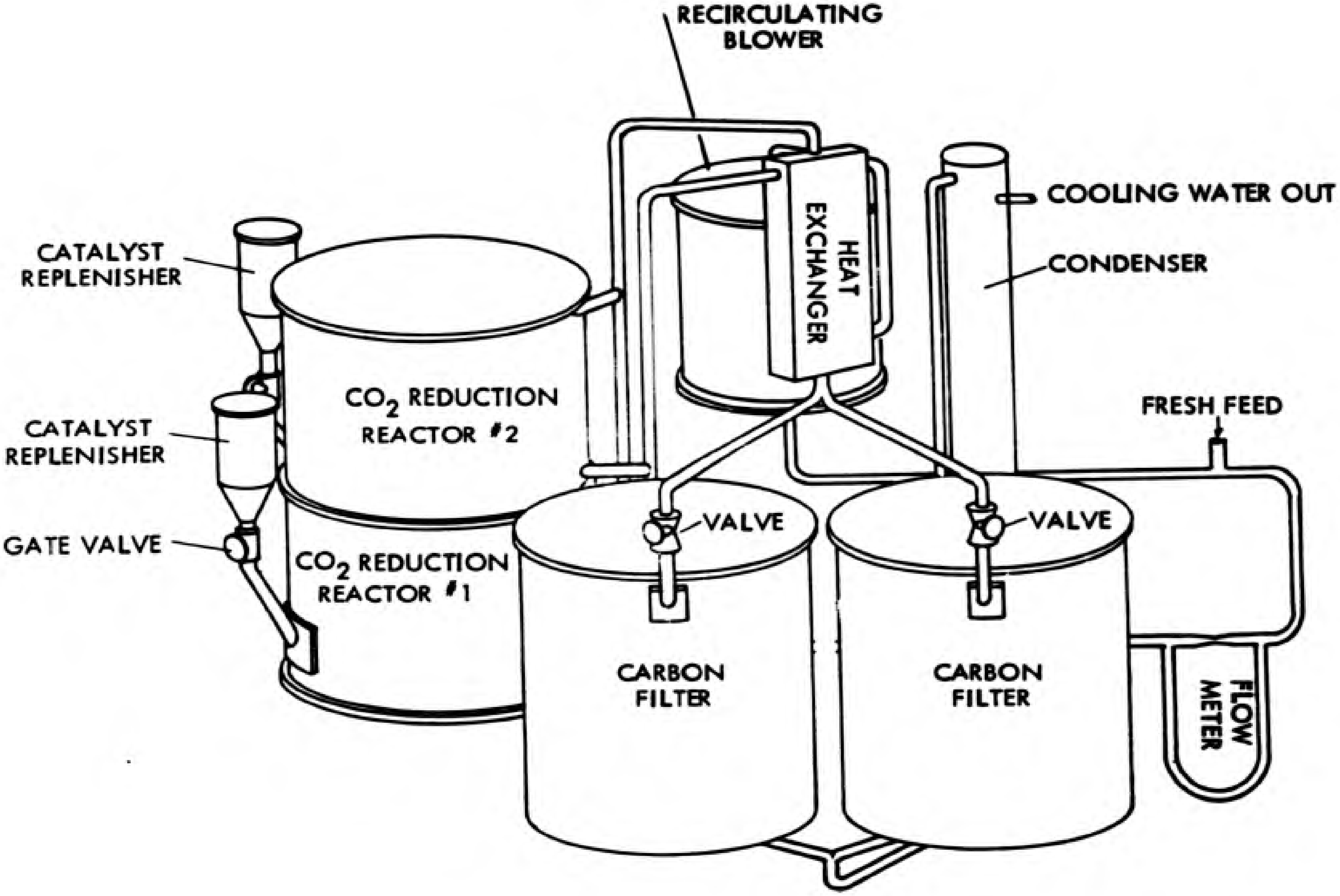


FIGURE 8-1A

REACTOR FOR 100 MAN CAPACITY SYSTEM

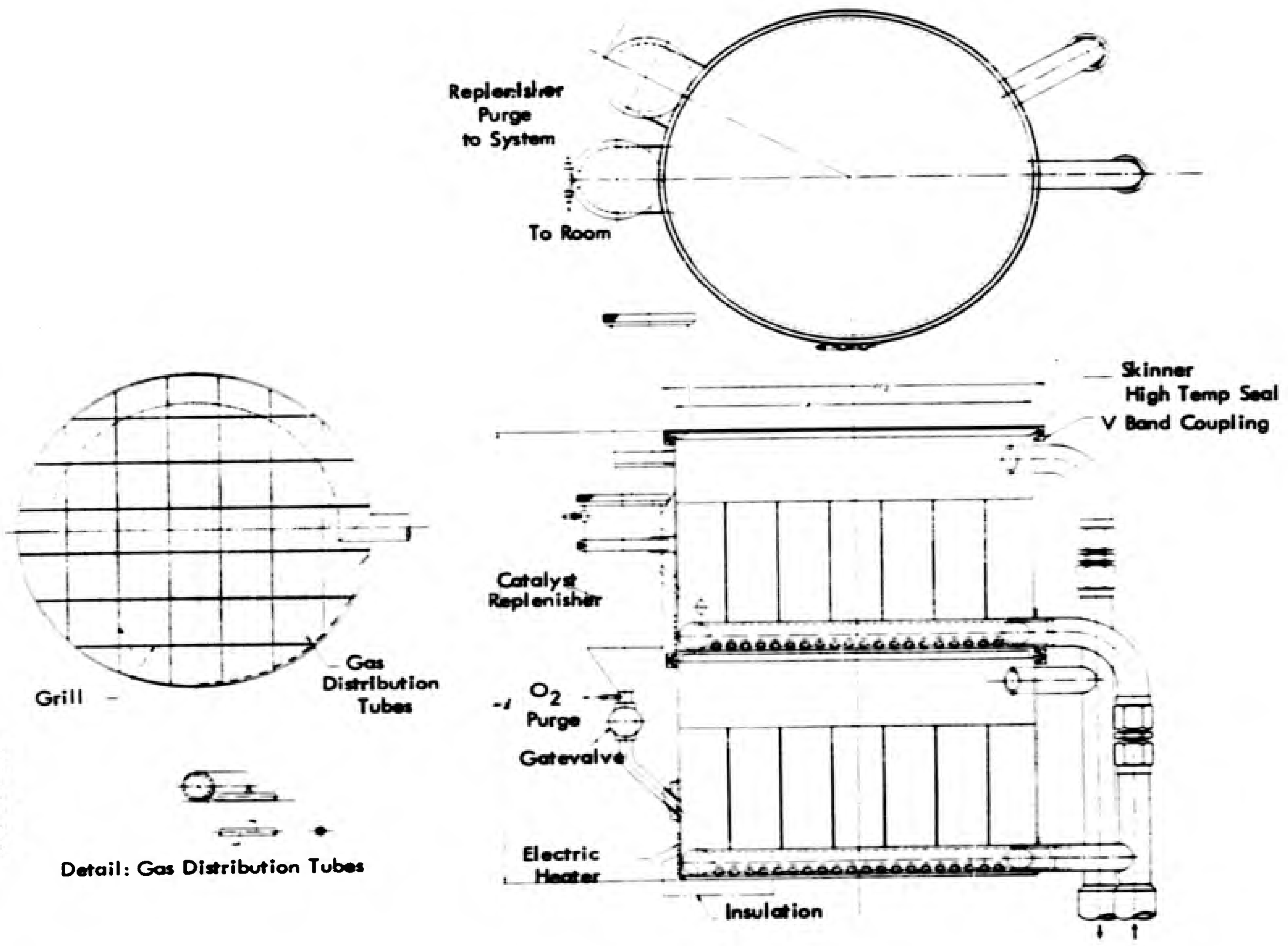


FIGURE 8-2

orifices which are sized to give a pressure drop of about 4" of water at normal flow rates. This will tend to ensure uniform flow through each orifice in spite of local temporary variations in bed pressure. The orifices are placed on the under sides of the tubes and are recessed to minimize the possibility of orifice stoppage by catalyst intrusion into the opening.

Provision is made for adding catalyst to the bed while the equipment is in operation. To prevent escape of reaction gases into the submarine, and to prevent the introduction of nitrogen into the system, a purging system is provided. After the catalyst is loaded into the catalyst induction device, it is purged with oxygen, the purge gases being vented into the submarine atmosphere. The catalyst is then introduced into the reactor and the induction valve closed. The induction chamber is again purged with oxygen, the purge gases being vented into the system. This purging of oxygen into the system will consume some hydrogen, but this is of no particular consequence since both gases can be regenerated by the electrolytic cell. The induction chamber can now be opened for refilling with catalyst.

The temperature of the reactor is regulated by electric heaters. The reaction taking place in the reactor is exothermic, but not sufficiently so to make up for the losses from the reactor to the environment and for losses due to the fact that the recycle gases are cooler when they enter the reactors than when they leave. A heat balance has been made on the reactor using the following assumptions:

(a) The reactor operates at 1100°F.
(b) The temperature of the incoming reaction gases is 908°F.
(c) The temperature of the gases leaving the reactor is 1100°F.
(d) The reactor is insulated with 3" of material having a conductivity of .04 BTU/Hr/sq ft/ft/°F.

Using these assumptions the following heat balance is obtained.

Heat generated in the reactor (100 man crew) - BTU/Hr	= 9,450
Heat lost to surroundings - BTU/Hr	= 3,180
Heat supplied to reaction gases - BTU/Hr	= 11,502
Net heat requirement - BTU/Hr	= 5,232
Power required for heater - Kw	= 1.53

8.5.3 The Heat Exchanger

In order to minimize carbon filter problems, it is desirable to filter the gases after they have been cooled, rather than when they are hot. One possibility is to place the heat exchanger between the reactor and filter, so that the reaction gases are cooled to about 300°F before entering the filter. The feasibility of operating in this way depends on whether or not it is possible to pass the carbon through the heat exchanger without fouling it in a short time. There is some evidence that this is feasible. During experimental run 14 about 10 grams of carbon was collected from the bottom of the heat exchanger. This was a shell and tube exchanger with the gases coming from the reactor passing through the tubes. This amount of carbon had passed through the tubes without appreciable fouling. It is believed that the heat exchanger and carbon removal problems can be finally and definitely solved only after additional experimentation. A great deal depends on how easily the carbon can be removed from the catalyst.

The heat exchanger designed for this service is presented in Figure 8-3. It is a plate and fin type exchanger having the dimensions of 3" x 6" x 15". On the hot side the gases pass directly through the length of the exchanger, while on the cold side the gases make three passes across the exchanger. This unit was designed for an effectiveness of 0.8, in accordance with the principles of Kay and London (Reference 11).

In order to minimize carbon deposition in the heat exchanger it is placed in a vertical position and the hot gases passed from top to bottom. If the carbon deposition problem turns out to be serious, it is always possible to arrange to clean the passages periodically without interrupting the operation of the equipment. This can be done by passing a wire brush through each passage at regular intervals, or as required.

The actual pressure drop through this heat exchanger is calculated to be about 0.5 inches of water on each side. However, in order to allow for manifolding and other miscellaneous losses, a conservative value of 3" of water was assumed for each side.

HEAT EXCHANGER FOR 100 MAN CAPACITY SYSTEM

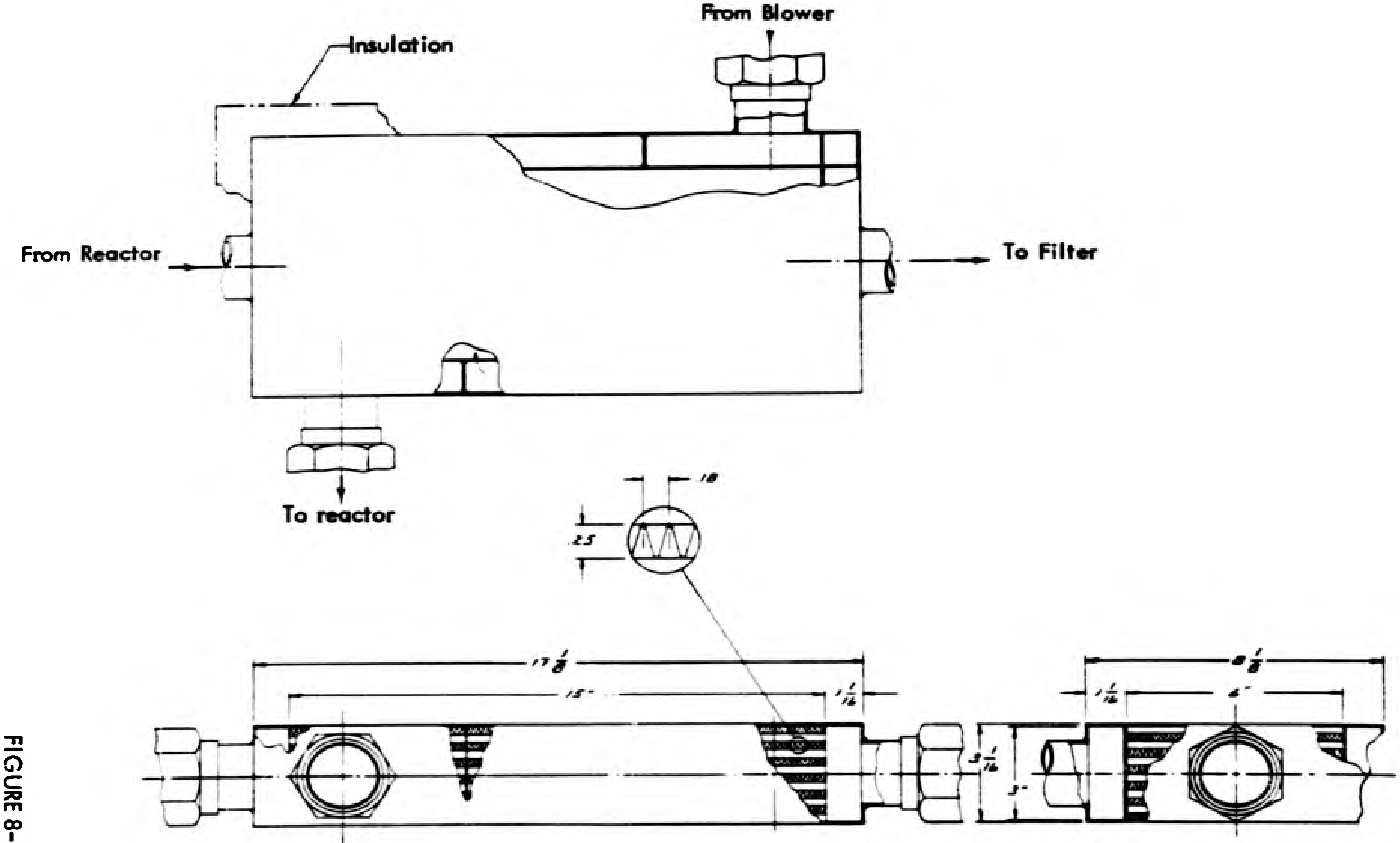


FIGURE 8-3

8.5.4 The Filter

The design of a filtering arrangement to be placed after the heat exchanger is shown in Figure 8-4. It consists of two chambers with valving arrangements so that the reaction gases containing the carbon can be passed through either chamber or both at once. Each chamber contains a removable cannister containing a filter bed in the bottom.

In normal operation the reaction gases containing the carbon would be routed through one of the chambers until the cannister contained the desired amount of carbon. The gas flow would then be switched to the other chamber. The chamber containing the full cannister would then be purged with oxygen, the purge gases being bled into the system. The chamber would then be opened by removing the top and the cannister removed. The cannister would be replaced by an empty one. The chamber would again be purged with oxygen, the purge gases being bled into the submarine atmosphere. In order to avoid explosion hazards that might result from the large amount of oxygen that would be introduced into the system if an oxygen filled chamber were suddenly opened to the system, the chamber is next purged from the system to the system, thus gradually replacing the oxygen with recycle gas. The chamber is now ready for re-use.

The valves proposed for use with this equipment have rubber to metal closing surfaces. It is expected that these valves will operate satisfactorily under conditions where some carbon and possibly traces of catalyst may be present on the closing surfaces.

8.5.5 The Condenser

A drawing of the condenser is presented in Figure 8-5. It is based on an exit gas flow rate of 33.6 cu ft/min. STP and the removal of .146 lb of water per minute. The total heat transfer is 16,500 BTU/Hr, of which 8,940 is latent heat of condensation and 7,500 BTU is sensible heat of the recycle gases. The condenser is designed for an exit temperature of 90°F under the extreme condition where the temperature of the water is as high as 80°F. The increase in cooling water temperature is 10°F, corresponding to a cooling water flow rate of 1650 lb/hr for the extreme condition.

The condenser is a shell and tube type, consisting of a shell having headers supporting a tube bundle 3 feet long consisting of 21 tubes each 3/8 O.D. with

CARBON FILTER FOR 100 MAN CAPACITY SYSTEM

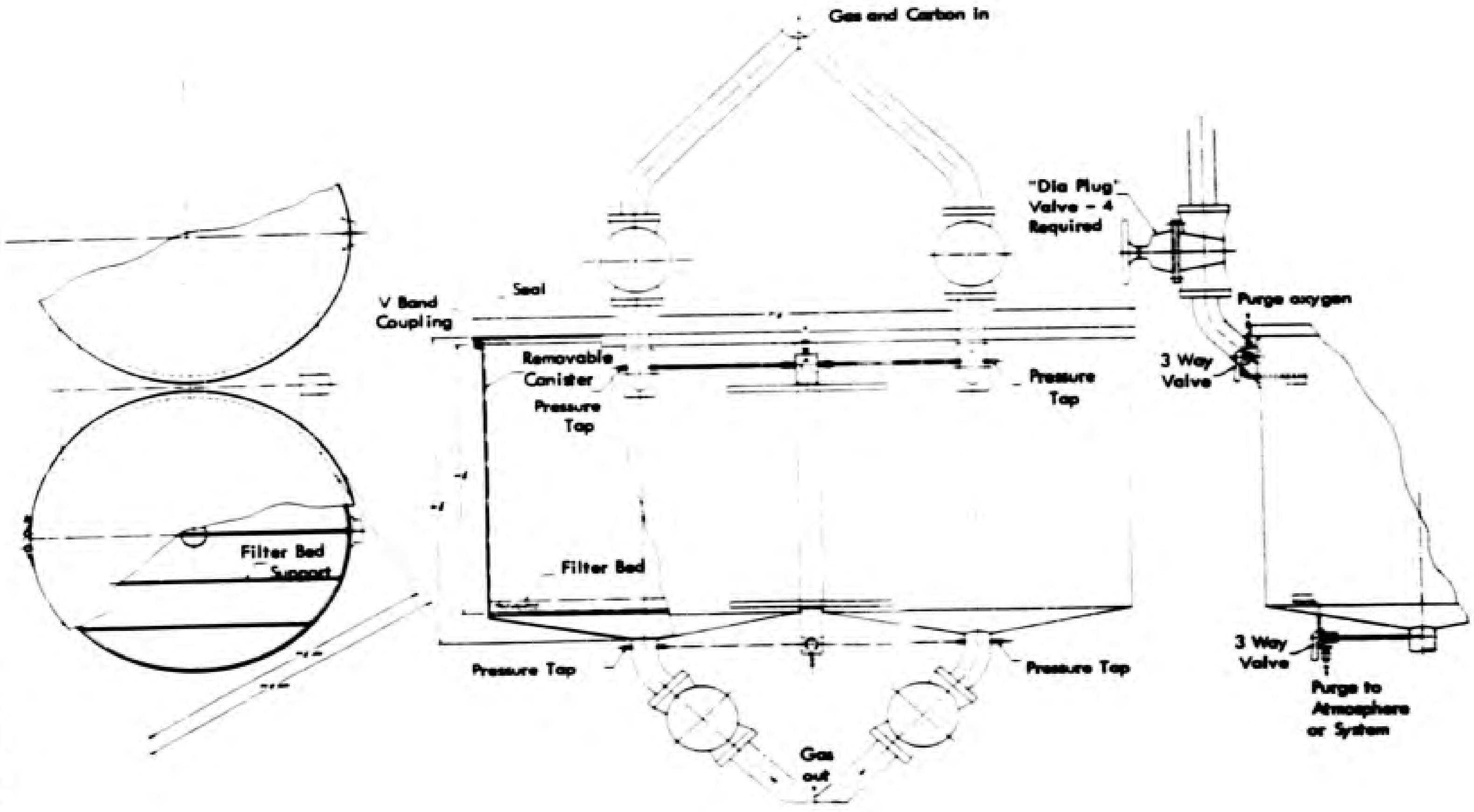


FIGURE 8-4

CONDENSER FOR 100 MAN CAPACITY SYSTEM

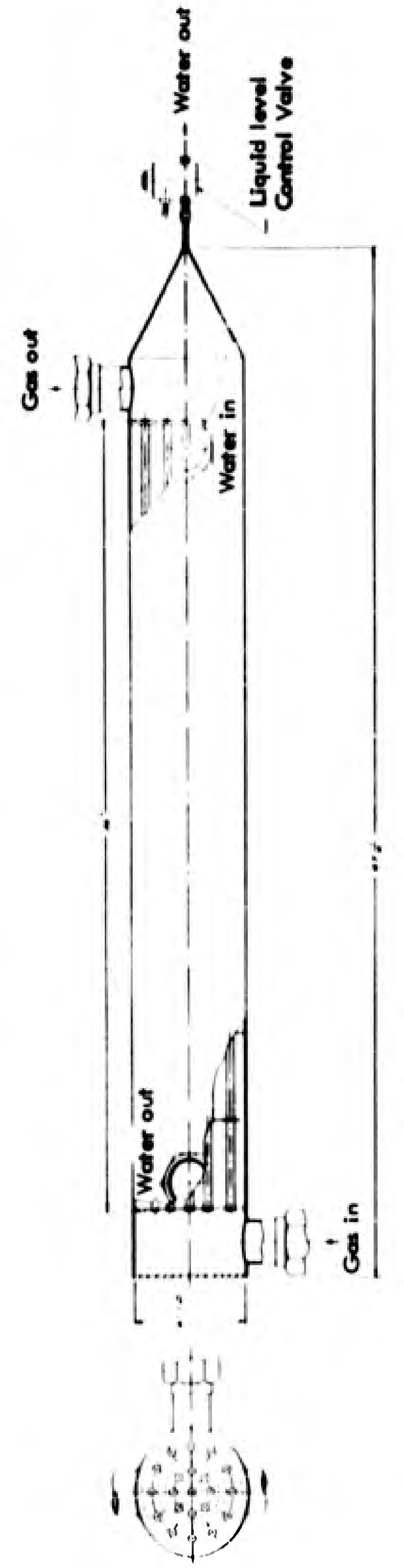


FIGURE 8-5

24 gauge walls. Provision is made for automatically withdrawing water from the bottom as it accumulates.

8.5.6 The Recirculating Pump

The recirculating pump must deliver 33.6 cu ft of gas at standard temperature and pressure (32°F and one atmosphere) at a pressure head of about 36" of water. An oil sealed pump is undesirable because of oil contamination of the recycle gases. A blower, appears to be the best solution, although most blowers are not able to generate the necessary pressure head. One blower has been found, however, that appears to have the necessary capability. This is a Rotron Model LRPU Type A6-120005 blower; a drawing of how this would be incorporated into the system is shown in Figure 8-6. In order to avoid shaft sealing problems, the motor and blower are both inside the sealed system. The manufacturer's performance and power consumption curves on this blower are shown in Figure 8-7.

It is estimated that the blower motor will consume about 600 watts. Since the motor will necessarily be cooled by the recycle gases, it follows that all of the power consumed by the blower will be reflected as a temperature rise in the recycle gas. It is estimated that this temperature rise will be 46°F.

8.5.7 Controls for the 100 Man Carbon Dioxide Reduction System

A schematic of the proposed control system is shown in Figure 8-8. The temperature of the reactor is controlled by regulating the electric current supplied to the reactor heater. The regulator responds to the information supplied by thermocouples in the two reactor chambers.

Pressure probes are provided on each side of the filter, so that the filter can be changed if the pressure drop through the filter becomes excessive.

The flow of cooling water to the condenser is regulated by a thermocouple in the cooling water outlet. In this way the temperature of the cooling water outlet can be kept at any desired value that is above the cooling water inlet temperature. The water removal from the condenser sump is controlled by a valve that acts on information supplied by two liquid level sensors in the sump. If liquid level reaches the top sensor the flow is increased, if it reaches the lower sensor, the flow is reduced.

RECIRCULATING PUMP FOR 100 MAN CAPACITY SYSTEM

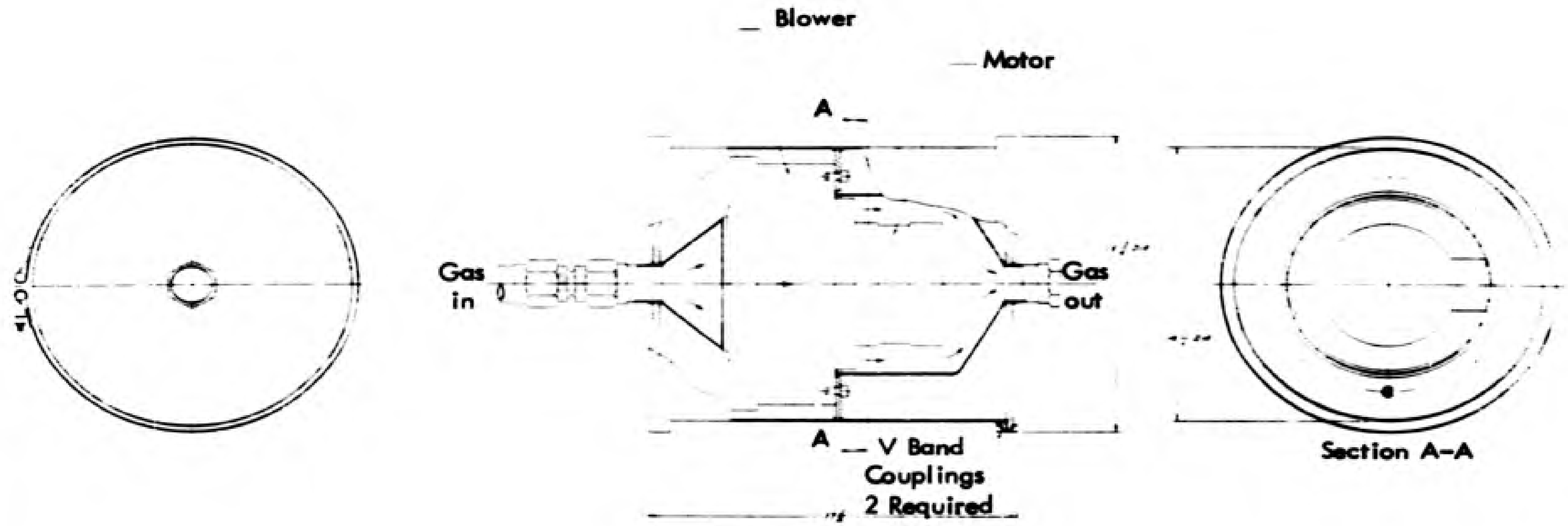


FIGURE 8-6

PERFORMANCE OF ROTRON BLOWER
MODEL LRPU- TYPE A6-120005

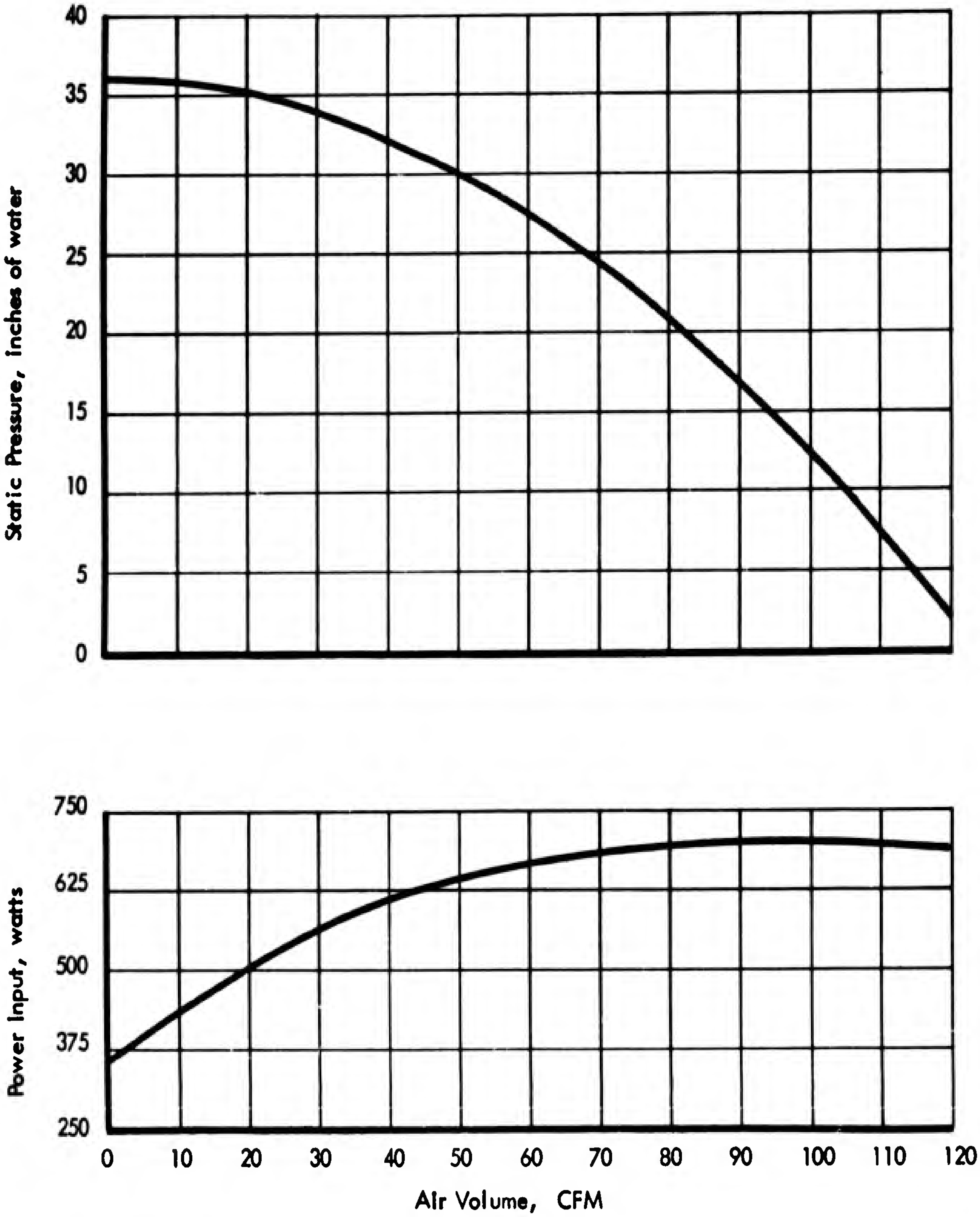


FIGURE 8-7

CONTROL SCHEMATIC FOR 100 MAN CO_2 REDUCTION EQUIPMENT

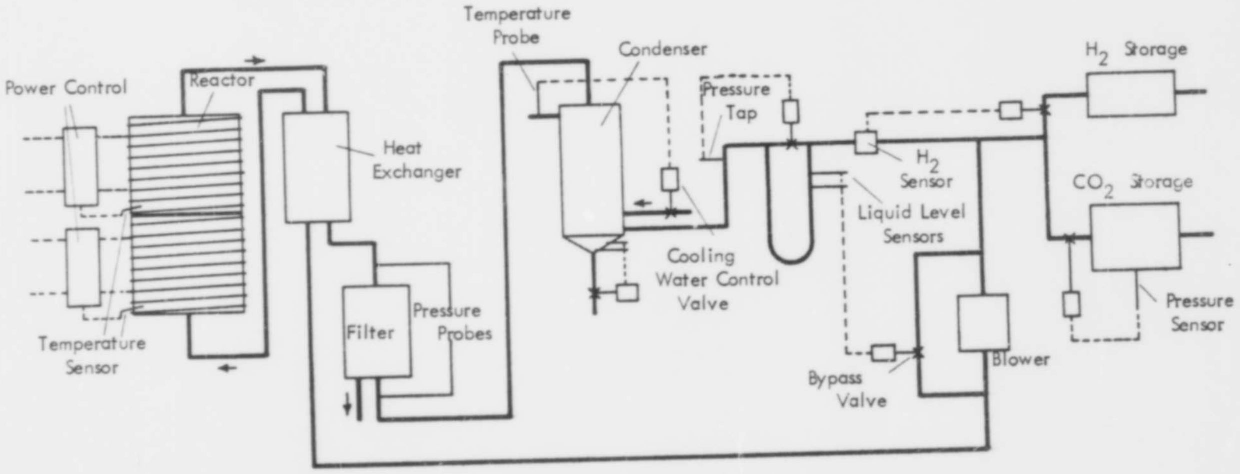


FIGURE 8-8

The recycle rate is controlled by a valve in the blower by-pass line. This valve acts on information supplied by liquid level sensors in the manometer of the flowmeter that measures the recycle rate. If the manometer liquid level reaches the upper sensor the by-pass flow is increased, decreasing the recycle rate. Conversely, if the liquid level reaches the lower sensor, the by-pass flow is decreased, increasing the recycle rate. The recycle rate is used to control the reaction rate in the system. This makes it necessary to change the level of recycle rate to correspond to the amount of carbon dioxide that is being produced. This is done by changing the orifice opening in the flowmeter. The flowmeter orifice opening is regulated to maintain the system pressure at the desired value by making the orifice opening respond to information supplied by a pressure tap in the system flow line.

The hydrogen flow to the system is controlled by a valve that acts on information supplied by a hydrogen sensor in the recycle gas line. If hydrogen is low in the recycle gas the hydrogen flow is increased and vice versa. Although not shown in the figure, the output of the electrolytic cell producing hydrogen and oxygen would be controlled by the pressure in the hydrogen storage tanks. If stored oxygen is used to correct the imbalance caused by the RQ problem, then the oxygen concentration in the submarine atmosphere would be controlled by adding supplemental oxygen.

The flow of carbon dioxide is controlled by the pressure in the carbon dioxide storage tank. This means that the system will reduce all the carbon dioxide that is supplied to it by the carbon dioxide removal equipment on the submarine.

8.5.8 System Consumption Estimates

Estimates have been made of the cost of carrying the 100 man capacity system on a submarine in terms of weight, volume, power consumption, and material consumption.

Weight and volume estimates on the various components of the system are presented in Table 8-3. The volumes quoted are those actually occupied by the equipment, including insulation. No attempt has been made to estimate the volume that would be rendered unusable by the installation of the equipment, since this would involve a number of unknown factors.

Table 8-3

ESTIMATED WEIGHT AND VOLUME DATA ON A 100 MAN CAPACITY SYSTEM

Component	Weight-lbs	Volume-cu.ft.
Reactor	156.8	12.8
Heat Exchanger	16.4	0.6
Filter	108.9	13.1
Condenser	22.8	0.8
Pump	69.5	1.9
Flow Meter	10.0	0.2
Lines	46.7	0.8
Controls	24.0	0.5
TOTAL	455.1	30.7

The power consumption shown in Figure 8-1 is 1.53 Kw for the reactor heater and 0.6 Kw for the recirculating blower. Allowing some power consumption for controls, etc., the total is estimated at 2.5 Kw.

The only material consumed by the system is catalyst. Unfortunately, sufficient life data are not available for making a realistic estimate of catalyst consumption. Literature data show that carbonyl iron powder is capable of producing up to 112 lbs of carbon per pound of catalyst in a reaction of this type (Reference 3). If such a ratio of carbon to catalyst could be achieved, the consumption of catalyst would be 36.6 pounds for a 100 man capacity system on a 60 day cruise. While it is likely that the actual catalyst consumption will be somewhat higher due to the carryover of some catalyst with the carbon, nevertheless, it is expected that the consumption of catalyst will be nominal.

9.0 CONCLUSIONS

On the basis of the data and discussion presented in this report, the following conclusions are believed to be justified.

(1) The current practice of venting hydrogen and carbon dioxide overboard from submarines represents a potentially ser us detection hazard.

(2) There are numerous problems associated with discharging waste products overborad from a deep operating submarine. Such a system would make a potentially noisy compressor unnecessary and would eliminate the flooding hazard of associated piping and open sea connections.

(3) It is entirely feasible to continuously react carbon dioxide with hydrogen to produce carbon and water, utilizing a fluidized catalyst bed for continuous removal of carbon.

(4) Carbonyl iron powder is a satisfactory catalyst for this operation.

(5) Reaction rates increase with temperature, but tend to level off at 1200 to 1300°F.

(6) The recycle gas hydrogen/oxygen atom ratio (H/O) for maximum reaction rate varies with the catalyst and has a value of about four for carbonyl iron at 1100°F.

(7) Reaction rate is approximately a linear function of recycle rate up to the point where the catalyst can no longer approximately bring the recycle gases to equilibrium on each pass.

(8) Completely drying the recycle gas increases the reaction rate up to 100%, depending on reaction conditions.

(9) The imbalance between carbon dioxide and hydrogen, resulting from the fact that the respiratory quotient is less than one, is best corrected by carrying about 15% of the required respiratory oxygen in the elementary form stored in tanks.

(10) The equipment required to reduce the carbon dioxide produced by a 100 man crew would weigh about 455 lbs and occupy a volume of 31 cu ft. The consumption of power and materials is nominal.

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The Reduction of Carbon Dioxide Using A Fluidized Catalyst Bed - Final Report
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Unclassified

Tests were conducted on a one man capacity CO_2 Reduction Oxygen regeneration unit. Various catalysts for the reaction were evaluated. Carbonyl iron was found to be a very satisfactory catalyst for the reaction. A preliminary design of a 100 man capacity carbon dioxide in this report. This system has a weight of 455 lbs and a volume of 31 cu ft. Power consumption of this unit is 2.5 Kw.

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2. Oxygen Reduction

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